

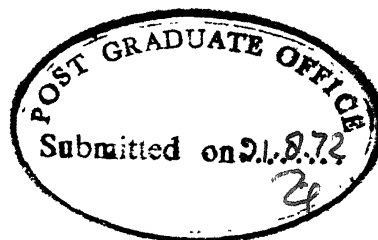
DESIGN AND FABRICATION OF A LIQUID METAL SOLUTION CALORIMETER AND THE DETERMINATION OF HEAT OF SOLUTION OF LEAD IN BISMUTH-LEAD-TIN ALLOY

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

BY
BHUPENDRA KUMAR GUPTA

to the


**DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
AUGUST 1972**



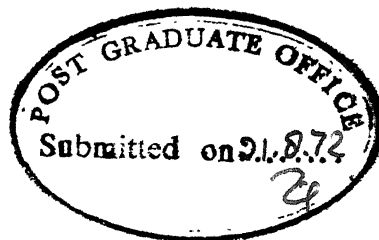
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CERTIFICATE

This is to certify that the work entitled "Design and fabrication of a liquid metal solution calorimeter and the determination of heat of solution of lead in bismuth-tin-lead alloys" has been carried out by Mr. Bhupendra Kumar Gupta under my supervision and that this work has not been submitted elsewhere for a degree.


A.K. Jena
Assistant Professor
Department of Metallurgical Engineering
Indian Institute of Technology
Kanpur.


POST GRADUATE OFFICE
This thesis has been approved
for the award of the Degree of
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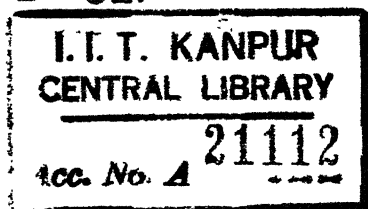
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ACKNOWLEDGEMENT

The author wishes to express his deep sense of gratitude to Dr. A.K. Jena for his invaluable guidance and encouragement throughout this study.

Thanks are due to Mr. K.P. Mukherjee for his help in the experimental work. Thanks are also due to many of friends who have helped directly or indirectly.

Last but not least, thanks are due to Mr. R.N. Srivastava for his neat and good typing of this thesis.

ABSTRACT

A liquid metal solution calorimeter has been designed and fabricated. It is capable of measuring heat effect on dissolution of various metals in liquid metal solvents with an accuracy of $\pm 0.8\%$. The calorimeter is described in detail and the technique employed in its operation is fully explained. The performance of the equipment and the results obtained are critically evaluated. The partial gram-atomic enthalpy of lead relative to solid lead in the bismuth-tin alloys has been measured as the function of composition of lead at $X_{\text{Sn}}/X_{\text{Bi}} = 1.5$. The results have been analysed on the basis of statistical models of solutions.

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Chapter I

INTRODUCTION

The values of free-energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes which accompany metallic reactions are parameters of importance in metallurgy. In the field of alloy theory it is necessary to know these parameters to understand and predict the behavior of multicomponent systems. There are various methods available for the measurement of these parameters. However, the calorimetric methods produce data which can be directly and unambiguously related to enthalpy changes. The liquid-metal solution calorimetric technique has the additional advantage of yielding precise data. It was, therefore, undertaken to design and fabricate a liquid-metal solution calorimeter. In order to demonstrate the applicability of this technique, the heat of solution of lead in Bi-Sn-Pb alloys has been measured.

Chapter II

PREVIOUS WORK

2.1. Available methods for measurement of thermodynamic properties

Various methods available for the determination of thermodynamic properties and other associated parameters can be divided into four categories; (i) E.m.f. measurement, (ii) Vapour pressure measurement, (iii) Chemical equilibria or equilibrium constant measurement, and (iv) Calorimetric measurement.

Galvanic cells are used to measure the difference in e.m.f. between an alloy and one of its pure constituents. This gives the free-energy change of the component. The values of enthalpy changes are obtained from the temperature co-efficient of the e.m.f. by the following equation⁽⁹⁾,

$$\Delta H = - n F \left[E - T \frac{\partial E}{\partial T} \right] \quad 2.1.1$$

where n = number of electrons involved in reaction

F = Faraday's constant

E = e.m.f. of the cell

T = temperature in $^{\circ}\text{K}$.

However it is difficult to obtain reversible cells and relatively small errors in the e.m.f. measurements can result in large errors in the derived values of the enthalpy changes. This is because of the presence of the first derivative of the e.m.f. in Eq. 2.1.1. The e.m.f. method is therefore found to be unsuitable for measurement of enthalpy changes.

Vapour pressure measurements lead to the determination of enthalpy changes by Claperyon's equation. Even though the vapour pressure data may be precise, the experimental conditions may be such as to render their accurate interpretation difficult⁽³⁾. In practice, the equilibrium technique is found suitable for free-energy changes only⁽²²⁾. The accuracy with which enthalpy and entropy changes can be deduced from the equilibrium measurement is unsatisfactory, as the calculation involve temperature coefficient of the equilibrium constant. By contrast, the calorimetric technique is relatively simple and is a direct method of determining enthalpy changes.

2.2. Calorimetric techniques

A calorimeter is, in principle an instrument which measures heat changes accompanying a process or a reaction. The reaction to be investigated is carried out in the calorimeter of known heat capacity and the heat effect is determined by measuring the change of temperature of the calorimeter. Since the temperature changes can be measured very precisely, the integral energy changes of the reaction can be obtained accurately. Calorimeters used by various investigators may be classified on the basis of the behavior of the substance under investigation.

- (i) Drop calorimeter^(1,5,6,7,23)
- (ii) Heating calorimeter^(9,10)
- (iii) Reaction calorimeter^(1,2,5,21)
- (iv) Solution calorimeter^(10,11,12,21)

In a Drop calorimeter the specimen is dropped from a higher temperature to a calorimeter at lower temperature and is allowed to cool.

temperature of the added melts, oxidation of the liquid metals and imperfect mixing. This method also requires large quantities of pure metals which is uneconomical.

The solution calorimeters employ a dissolution reaction as the principle mechanism of operation. For the measurement of energy changes accompanying solid state processes and reactions which are slow, the solution calorimeters have many advantages. Acid solution calorimeters use acids as the solvent for the dissolution reaction⁽¹⁴⁾. These are at present hardly used because of its following drawbacks:

- (i) It is possible to get irreproducible oxidation states.
- (ii) The heats of solution are large compared with the heats of formation in metallic systems.
- (iii) Final reaction products are often uncertain.

The use of liquid metal solvents eliminates many disadvantages of acid-solution calorimetry. The advantages of the liquid-metal solution calorimeter can be summarised as follows:

- (i) The dissolution of a solid metal or alloy in a metallic melt is very fast.
- (ii) The final state of the solution is well defined and reproducible.
- (iii) Gaseous products of reactions are not involved.
- (iv) The heat of solution in liquid metals are of the same order as the heats of formation to be determined. It is this consideration that has made metallic solution calorimetry most valuable for the accurate determination of enthalpy changes in metallic systems.

In a liquid metal solution calorimeter, the heat changes accompanying a dissolution reaction are measured. By alternately dissolving a material in its standard state (A^\ominus) and in any other state (A) in a

suitable solvent under otherwise identical conditions, the difference in enthalpy between these two states, $\left[(H_A - H_{Ao}) = \Delta H_{(T)} \right]$, is obtained as the difference between the heat effects of the two dissolution processes.

2.3. Liquid metal solution calorimeter

In designing a liquid metal solution calorimeter unit the following criteria must be taken into consideration.

- (i) The main calorimetric unit must be contained in such a thermal environment in which heat transfer between the environment and the calorimetric unit occurs according to a known law. In other words, there should not be any unaccountable heat losses.
- (ii) The calorimeter must be contained in constant temperature environment.
- (iii) To avoid oxidation, calorimeter must be kept in vacuum or in an inert atmosphere.
- (iv) The temperature sensing devices must be accurate and reproducible.

The liquid metal solution calorimetric technique was first introduced by Ticknor and Bever⁽¹¹⁾ in 1952 at M.I.T. (U.S.A.). Since then several new designs and modifications of this calorimeter have been reported^(11-13,15,16,18-20,24-27). Table I and Figs. 1, 2 and 3 give details of some of the important liquid metal solution calorimeters developed so far.

The calculation of the heat effect of an addition is made in two parts, (i) an observed temperature change (at a given time after completing of reaction), is noted and the heat effect corresponding to this temperature change is evaluated, (ii) during this time all of the heat of reaction does not remain in the calorimeter. Therefore a correction has to be made

Table I - Details of Some Liquid-metal Solution Calorimeters

Details	Bever et al ^(11,15)	Kleppa ⁽¹²⁾	Hultgren et al ⁽¹⁸⁾	Leach et al ^(16,17)
1. Thermostat	Eutectic mixture of Na, K & Li nitrates	Aluminium block and radiation shields	Ni plated copper block	Mixture of Na & K nitrates
2. Temperature range	240-450°C	250-500°C	250-500°C	240-500°C
3. Temperature control	Electronic*, $\pm 0.002^\circ\text{C}$	On-off controller and radiation shields, $\pm 0.01^\circ\text{C}$	Proportional controller and radiation shields, $\pm 0.001^\circ\text{C}$	Electronic*, $\pm 0.001^\circ\text{C}$
4. Calorimetric unit	Dewar flask	Graphite crucible	Mo-crucible	Mo-crucible
5. Stirrer	Helical Glass stirrer (Rotating)	Graphite inverted cup (Rotating)	Mo-impeller (Rotating)	Mo-stirrer (Oscillating)
6. Temperature measuring unit	Cr/Al thermocouple put inside invar well	Cr/Al thermocouple	Copper-Constantan thermocouple	Cr/Al thermocouple in the hollow stirrer
7. Sensitivity of temperature measurement	0.005°C	0.001°C	0.0025°C	0.0010°C
8. Calibration	Chemical**	Electrical	Chemical	Chemical
9. Environment surrounding calorimeter	Vacuum, 10^{-3} to 10^{-4} mm of Hg	Argon gas	Vacuum, 10^{-4} mm of Hg	Vacuum, 10^{-4} to 10^{-5} mm of Hg
10. Accuracy of the measurement	± 0.2 to $\pm 2\%$	$\pm 1\%$	$\pm 2\%$	$\pm 0.25\%$

* Electronic control system consists of Pt. resistance thermometer, Reflection galvanometer, photocell, Amplifier and Transducer.

** Measuring heat effect of known heat content.

depending on the heat transfer coefficient. The accuracy of measurement is therefore limited by the uncertainty in the heat exchanged with the environment during the reaction period. This arises from the uncertainty in the value of heat transfer coefficient. In the design of the liquid metal solution calorimeter the primary aim is to obtain a constant heat transfer coefficient.

In Bever calorimeter⁽¹⁵⁾, the heat transfer coefficient 'k' is found to be time dependent and also the all glass container is rather fragile. A further development of Bever calorimeter is reported by Kravitz and Leach⁽¹⁶⁾, and Jena and Leach⁽¹⁷⁾ who obtained 'k' values independent of time. However the design is rather complicated and expensive to fabricate. The calorimeter developed by Kleppa⁽¹²⁾ is rather unsatisfactory because of (i) the calibration errors due to variation in electrical power input, (ii) the measurement of the temperature of the calorimeter in its wall rather than in the solvent bath and (iii) poor stirring.

In the Hultgren⁽¹⁸⁾ calorimeter it is found that during the cooling period of the calorimeter the heat transfer coefficient varies with time. The deviation from 'Linear' Newtonian conditions in the value of K is dealt with by ascribing a time dependence of the form:

$$t(1 - \frac{a}{2} t - \frac{b}{2} t^2).$$

2.4. Energetics of dilute solutions

Energetics of dilute solutions are of interest in understanding the constitution of dilute multicomponent solutions and in evaluating the thermodynamic properties of these solutions. Data on the partial gram-atomic

enthalpies can be analysed on the basis of statistical theories to yield information about the constitution of solutions. The dilute binary solutions have been investigated by Oriani and Murphy⁽²⁸⁾, Jena and Bever^(29,30), Jena and Leach⁽³¹⁾ etc. A review of such work has been recently reported by Jena⁽⁴³⁾. Work on ternary dilute solutions has been done by Kravitz and Leach⁽¹⁶⁾ and Jena, Smith and Bever⁽³²⁾. The study of Jena et al on the dilute solution of Au in Bi-Sn indicates that the energy of Au-Au bond in solution is approximately 12% less than from those calculated on the basis of the regular solution theory. However the deviation from regular solution theory is believed to be due to change in coordination number of Au because of its smaller size. Since the atomic volumes of elements bismuth and tin at 623°K, are 9.6 pct. and 61 pct.⁽³³⁾ higher than that of gold, the value of coordination number of gold in solution may be expected to be different from that of the solvent.

The binary Bi-Sn solutions behave ideally and the heat of solution of lead in Bi⁽³⁴⁾ and Sn⁽¹²⁾ at 700°K are -840 and 1345 cal/g-atom respectively. No data is available on the heat of solution of lead in Bi-Sn-Pb ternary alloys. Since the atomic volumes of Bi, Sn and Pb are 35.4, 25.3 and 30.3 Å³^(36,37) respectively, the Bi-Sn-Pb ternary alloys are expected to be simpler than the Bi-Sn-Au ternary alloys.

Chapter III

EXPERIMENTAL TECHNIQUE

3.1. Theoretical consideration

A liquid metal solution calorimeter consists of a solvent bath maintained in a constant temperature environment. At a particular instance, let the temperatures of the environment and the container of the solvent bath be T_s and T respectively such that $T_s > T$. The rate of heat exchange is given by the following expression,

$$\dot{q} = K_R(T_s^4 - T^4) + K_C(T_s - T) + h(T_s - T) \quad 3.1.1$$

where K_R , K_C and h are constants corresponding to heat transfer by radiation, conduction and convection respectively. Writing $(T_s - T) = \Delta T$ and expanding the term $(T_s^4 - T^4)$, the Eq. 3.1.1 becomes

$$\dot{q} = 4T_s^3 K_R \left[1 - \frac{3}{2}\left(\frac{\Delta T}{T_s}\right) + \left(\frac{\Delta T}{T_s}\right)^2 - \frac{1}{4}\left(\frac{\Delta T}{T_s}\right)^3 \right] \Delta T + K_C \Delta T + h \Delta T \quad 3.1.2$$

ΔT is often of the order of $\pm 0.5^\circ\text{C}$. Taking 600°K for T_s the term in the square bracket is reduced to 1 ± 0.001 . Therefore, we can neglect the terms containing $\left(\frac{\Delta T}{T_s}\right)$. The Eq. 3.1.2 becomes

$$\dot{q} = K(T_s - T) \quad 3.1.3$$

$$\text{where } K = (4T_s^3 K_R + K_C + h) = \text{a constant} \quad 3.1.4$$

The contribution due to K_C and h in Eq. 3.1.4 can be made negligible by maintaining vacuum and thermally insulating the environment from the solvent bath. Thus constant 'K' can be made independent of time.

When a specimen is added to the calorimeter the temperature of the solvent bath is changed as the specimen is at a temperature different from that of the bath. The temperature variation of the bath in a typical addition is shown in Fig. 4. It then follows that at a particular instant,

$$\frac{dq_{sp.}}{dt} + \frac{dq_{cal.}}{dt} = K(T_s - T) \quad 3.1.5$$

where $\frac{dq_{sp.}}{dt}$ = rate at which heat is absorbed by specimen

$\frac{dq_{cal.}}{dt}$ = rate at which heat is absorbed by calorimeter

and $K(T_s - T)$ = rate at which heat is received from the surrounding.

At equilibrium,

$$\frac{dq_{sp.}}{dt} = 0$$

and $T = T_e = \text{a constant.}$

Hence

$$\left(\frac{dq}{dt}\right)_e = K(T_s - T_e) \quad 3.1.6$$

Using Eq. 3.1.6, Eq. 3.1.5 reduces to

$$\left(\frac{dq_{cal.}}{dt}\right) = \left(\frac{dq}{dt}\right)_e + K(T_e - T) - \left(\frac{dq_{sp.}}{dt}\right) \quad 3.1.7$$

Also

$$\left(\frac{dq_{cal.}}{dt}\right) = \left(\frac{dq}{dt}\right)_e + C_p \frac{dT}{dt} \quad 3.1.8$$

where C_p = heat capacity of calorimeter at particular instant.

Substituting Eq. 3.1.8 in the Eq. 3.1.7, we get

$$\left(\frac{dq_{sp.}}{dt}\right) + C_p \frac{dT}{dt} = K(T_e - T) \quad 3.1.9$$

Integrating Eq. 3.1.9 corresponding to the temperature T and time t , we get

$$\int_{T_0}^T dq_{sp.} + \int_{T_e}^T C_p dT = \int_{t_0}^t K(T_e - T) dt \quad 3.1.10$$

But

$$\int_{T_0}^T dq_{sp.} = n_{sp.} \int_{T_0}^T C_{p_{sp.}} dT + n_{sp.} Q_{T_e} + \int_{T_e}^T n_{sp.} \bar{C}_{p_{sp.}(soln)} dT \quad 3.1.11$$

where Q_{T_e} = heat absorbed by a mole of specimen on solution at T_e

$n_{sp.}$ = number of moles of the specimen

T_0 = initial temperature of the specimen

$\bar{C}_{p_{sp.}(soln)}$ = partial gram-atomic heat-capacity of specimen in solution.

$$\int_{T_0}^T C_{p_{sp.}} dT = (H_{T_e} - H_{T_0})_{sp}$$

Substituting Eq. 3.1.11 in Eq. 3.1.10

$$n_{sp.} (H_{T_e} - H_{T_0})_{sp.} + n_{sp.} Q_{T_e} + \int_{T_e}^T \left[C_{p_{cal.}} + n_{sp.} \bar{C}_{p_{sp.}(soln)} \right] dT$$

$$= \int_{t_0}^t K(T_e - T) dt$$

Let us define C_{p_f} , the average final heat-capacity such that

$$\int_{T_e}^T [C_p + n_{sp.} \bar{C}_{p(soln)}] dT = C_{p_f} (T - T_e)$$

Then

$$n_{sp.} (H_{T_e} - H_{T_0})_{sp.} + n_{sp.} Q_{T_e} + C_{p_f} (T - T_e) = K \int_{t_0}^t (T_e - T) dt$$

3.1.12

Differentiating Eq. 3.1.12

$$C_{p_f} d \ln(T_e - T) = -K dt$$

$$\text{or} \quad d \ln(T_e - T) = -k dt$$

$$\text{where} \quad k C_{p_f} = K$$

3.1.13

$$\text{or} \quad \ln(T_e - T) = -kt + C$$

3.1.14

This equation shows that the heat transfer coefficient 'k' can be obtained for any addition from a plot of $\log_e(T_e - T)$ against 't'.
Eq. 3.1.12 can be rewritten after substituting Eq. 3.1.13 as follows,

$$Q_{T_e} = \frac{C_{p_f}}{n_{sp.}} \left[(T_e - T) + k \int_{t_0}^t (T_e - T) dt \right] - (H_{T_e} - H_{T_0})_{sp.} \quad 3.1.15$$

For a calibrating additions, where $Q_{T_e} = 0$, Eq. 3.1.15 gives

$$C_{p_f} = n_{sp.} (H_{T_e} - H_{T_0})_{sp.} / T_{corr.} \quad 3.1.16$$

$$\text{where } \Delta T_{corr.} = \left[(T_e - T) + k \int_{t_0}^t (T_e - T) dt \right] \quad 3.1.17$$

The heat capacity of the calorimeter ' C_{p_f} ' is obtained with the help of Eq. 3.1.16 by adding specimens of known heat effect. Knowing C_{p_f} , the heat of solution of any addition can be determined by using Eq. 3.1.15.

Usually a number of additions are made to a particular load of bath. If o, m, r --- represent the number of additions and $C_{p_f}^r$ is the value of C_{p_f} for the r^{th} addition, then $C_{p_f}^m$ can be calculated by following expression,

$$C_{p_f}^m = C_{p_f}^r + \sum_{i=1}^i \bar{C}_{p_i} (n_i^m - n_i^r) \quad 3.1.18$$

where n_i^r = number of moles of component 'i' in the crucible at the end of r^{th} addition
 \bar{C}_{p_i} = ^{partial} molar heat capacity of component 'i'.

3.2. Design and fabrication of calorimeter

The liquid metal solution calorimeter consists of a constant temperature environment maintained around a central calorimetric unit.

The space between the environment and the crucible containing liquid metal, is kept under vacuum in order to reduce the heat transfer coefficient and the oxidation of the solvent metal. The primary aim in designing this calorimeter has been to achieve a constant temperature environment, and a minimum and rational heat transfer coefficient. The description of the equipment is divided into the following sections,

- (i) The thermostat.
- (ii) The calorimetric unit.
- (iii) The vacuum system.
- (iv) The temperature measuring system.

3.2.1. The thermostat Previous workers in the field of liquid metal solution calorimetry have used the following thermostats;

- (i) Salt bath with electronic control system,
- (ii) Metal block with electronic control system, and
- (iii) Metal block with number of radiation shields and a simple proportional controller.

The first one is very complicated to fabricate and a number of practical difficulties are associated with its maintenance e.g. corrosion by salt bath etc. The electronic control system is very difficult to construct and expensive to instal and maintain. The last method is relatively simple and cheap. Therefore, this method was found suitable to instal for this liquid metal solution calorimeter. The theory of this method is based on the early work by Tian⁽³⁸⁾ on multiple enclosure thermostat. "If a thermostat consists of a central body surrounded by multiple enclosures, thermally insulated from the central body and each other, the temperature

fluctuation of the central body can be reduced substantially by locating the temperature controlling system at the outer most enclosure.* Assuming that the temperature fluctuations in the outermost enclosure is sinusoidal,

$$T_1 = T + \frac{E}{2} \sin 2\pi \gamma t \quad 3.2.1$$

where T = mean temperature of enclosure

T_1 = instantaneous temperature of the outermost enclosure
at any time t

E = amplitude of fluctuation of temperature

γ = frequency of oscillations.

Similarly the expression for temperature fluctuation in the second enclosure can be written as.

$$T_2 = T + \frac{E'}{2} \sin (2\pi \gamma t - \phi) \quad 3.2.2$$

where T_2 = the instantaneous temperature of enclosure

ϕ = phase lag in the temperature fluctuations between two
enclosures

E' = amplitude of fluctuation of temperature in the second
enclosure.

If K is the coefficient of heat transfer between these two enclosures, then the heat conducted from outer to inner enclosure follows well known differential equation,

$$K(T_1 - T_2) = C_2 \frac{dT_2}{dt} \quad 3.2.3$$

Now solving Eq. 3.2.1, 3.2.2 and 3.2.3 simultaneously, we get

$$\tan \phi = 2\pi \gamma \frac{C_2}{K} \quad 3.2.4a$$

$$\text{and} \quad E' = E \cos \phi \quad 3.2.4b$$

To reduce temperature fluctuation substantially in the second enclosure E' must be much less than E , which intern means that $\cos \phi$ is minimum.

But as $\cos \phi \rightarrow 0$, $\phi \rightarrow \pi/2$ and $\cos \phi = \frac{1}{\tan \phi}$.

Thus Eq. 3.2.4b can be written as

$$E' = E \frac{K}{2\pi \gamma C_2} \quad 3.2.5$$

The Eq. 3.2.5 sets the criteria for the design of thermostat. For maximum reduction in the temperature fluctuations, the following factors were taken into consideration,

- (i) Maximum heat capacity of the multiple enclosures C_2 .
- (ii) Minimum heat transfer between the enclosures.
- (iii) Maximum frequency of oscillations γ i.e. the maximum frequency of on-off of the controller.

The thermostat consists of a steel container which is 15" deep, and 9 sq. inches in cross section, and has a wall of thickness $\frac{3}{8}$ ". The container is chromium plated to prevent oxidation of mild steel container. The next enclosure is an aluminium cylinder; 7" in diameter, 11" deep with a wall thickness of $\frac{1}{4}$ ". The aluminium cylinder is thermally insulated from the steel container by placing alumina plates between them. The radiation shields consist of coaxial cylinders made up of $\frac{1}{8}$ " thick copper sheet. These radiation shields are supported on $\frac{1}{8}$ " thick stainless steel pins which are silver brazed to the radiation shields as shown in Fig. 5.

As stainless steel is a poor thermal conductor and the diameter of pins is very small, there will be very little thermal conduction between the enclosures.

The heating coils enclosed in grooved tiles are placed outside the steel shell. The electrical insulation between the coils and the steel container is provided by putting fireclay spacers between them. The furnace is enclosed in light-weight fireclay bricks (thermal conductivity 5×10^{-4} cal/sec/cm³/°C at 250°C). The gap between them is filled with magnesia powder. The whole system is enclosed in a cylinder of galvanised iron 24" in diameter, 30" deep with a wall thickness of $\frac{1}{8}$ ". The tiles were prepared from a mixture containing 40% fireclay greg, 20% fine fireclay and 40% china clay. The tiles were sintered at 1500°C for 6 hrs. A brass flange is used to cover the steel container. It is also provided with the heating tiles to heat the top of the calorimeter. The heating coils are connected to the variacs to draw the power at desired voltage. Ninety percent of the power is directly supplied through variacs and about 10% of the power (by top heater) is connected to the on-off controller. In order to maintain a temperature of 200-250°C, a current of 4.5 amps at 120 V was maintained in the heating coils at sides and 5 amps at 30 V in the heating coils at top and bottom. Thus the total power requirement was 1.4 KW.

The required temperature control is achieved by a on-off temperature controller (Leads & Northrup, Electromax.). A chromel/Alumel thermocouple is used to sense the temperature fluctuations at the outer steel shell. The thermocouple is housed in a ceramic well placed between the grooved tiles and steel shell. To avoid the effect of room temperature fluctuations, the cold junction of the thermocouple is maintained in a

Dewar flask packed with ground ice. The copper wires from cold junction are connected to the temperature controller. The controller is capable of giving a temperature control of $\pm 1^\circ\text{C}$. A calculation using Eq. 3.2.5 shows that a change of $\pm 1^\circ\text{C}$ in the outermost enclosure temperature, will give a temperature fluctuation of $\pm 0.001^\circ\text{C}$ at the centre of the calorimeter. But actual measurements showed that the temperature of the solvent bath in the central calorimetric unit was constant to $\pm 0.005^\circ\text{C}$ for a period of 20-30 minutes which is sufficient for an experiment.

3.2.2. The calorimetric unit: The calorimetric unit consists of a crucible, a solvent bath, stirrer and addition system. The 2" diameter and 3" deep crucible is fabricated out of stainless steel sheet of wall thickness 0.05". The crucible is placed in the centre of calorimeter on three 0.2" diameter and 3" high alumina rods which are inserted in the blind holes at the bottom of the steel shell.

Heat transfer between the crucible and the radiation shields can be analysed by considering them as two concentric spheres of diameter 2" and 8" respectively. It can be shown that the net heat transfer by radiation per second is given by,

$$q_{1-2} = A_1 \sigma (T_1^4 - T_2^4) \frac{1}{\frac{1}{e_1} + \frac{A_1}{A_2} \frac{1}{e_2} - \frac{A_1}{A_2}}$$

where A_1 = surface area of the crucible
 T_1 = absolute temperature of crucible
 e_1 = emissivity of the crucible
 and σ = radiation constant

The subscript 2 refers to the same parameters for the radiation shields.

In our system

$$\frac{A_1}{A_2} = \frac{1}{16}$$

Let

$$f(e) = \frac{1}{e_1} + \frac{A_1}{A_2} \left(\frac{1}{e_2} - 1 \right)$$

$$\text{or} \quad f(e) = \frac{1}{e_1} + \frac{1}{16} \left(\frac{1}{e_2} - 1 \right) \quad 3.2.6$$

It is obvious from Eq. 3.2.6 that $f(e)$ is more sensitive to variation in e_1 than that in e_2 . Therefore, maintenance of a bright surface on the crucible is definitely desirable to have minimum heat transfer. For this reason crucible is always given a good polish before it is used for any experiment.

The metal bath is stirred in order to obtain uniform temperature and composition, and to increase the rate of dissolution. The stirrer consists of 30" long and 0.25" diameter stainless steel rod. A 0.04" thick, 0.625" wide and 1.25" long stainless steel helical blade is spot welded to the end of this rod. About 3-4" of the rod near the blade is swaged to the diameter of 0.1" in order to reduce the heat loss through the stirrer. The stirrer rod passes through a self lubricated ball bearings fixed on the top of the aluminium cylinder and a double wilson seal (Fig. 6) brazed to the top of a stainless steel tube. The stirrer is connected to the rotating shaft by a rigid vacuum rubber tube so that the misalignment in the two metal shafts can be accommodated. The rotating motion is imparted by a synchronised, 1½ watts, 30 r.p.m. motor. The speed is increased to

100 r.p.m. by a step up pulley.(Fig. 6). The motor pulley arrangement and the ball bearings housing are mounted on an aluminium plate. The position of the aluminium plate support can be changed by moving the assembly along the hollow mild steel tube to which the aluminium plate is attached. The whole of the stirring system is fabricated so as to have maximum versatility. It has got three degree of freedom to adjust the position of stirrer in the centre of calorimeter.

The samples are added through a $\frac{1}{2}$ " diameter stainless steel tube which extends down to the top of the crucible. The stainless steel tube is also bent at two places so as to reduce the speed of the falling samples. A gate valve (Fig. 7) is attached to this stainless steel tube by O-ring seal. A 1" diameter pyrex tube is attached to the gate valve by an aluminium wilson seal (Fig. 8). The specimen is kept in a glass addition tube which is bent so that its closed end can be placed in a Dewar flask and can also be rotated with the use of a cone and socket ground glass joint. A ground glass vacuum valve is also attached to this tube so that before opening the gate valve the glass system can be evacuated.

3.2.3. The vacuum system: There are two reasons for enclosing the calorimeter in a vacuum system; one is to avoid convection and conduction through the air or gas surrounding the calorimeter and the other is to reduce oxidation of liquid metal in the calorimeter. The vacuum in the system is maintained by a rotating pump and a vacuum up to 20 to 50 μ is obtained by it. The vacuum in the system is measured by Vecco thermo-couple gauge.

The vacuum is maintained in the mild steel shell through 2" diameter stainless steel tube shown in Fig. 5. A copper adapter is silver brazed to this tube so that the vacuum rubber tube can easily be inserted over it. Vacuum seal at room temperature are made with O-rings fabricated out of neoprene rubber. The seal between the flange of the mild steel shell and the top brass flange is made with 11.975" I.D. O-ring seal. The flanges are water cooled. A number of small holes, about $\frac{1}{2}$ " in diameter, are made in the radiation shields to avoid blockade of the air passage for vacuum.

The seal at the end of the thermocouple tube is made by attaching a copper adapter with O-ring seal (Fig. 5). The gate valve in the addition system and double wilson seal in the stirring system are vacuum tight.

3.2.4. The temperature measuring unit: A 36 gauge fibre - glass insulated Chromel/Alumel thermocouple is used for the measurement of temperature. The hot junction^{bead} is made by striking an arc with mercury at 30 volts. The thermocouple is passed into the vacuum system through a small alumina tube (0.05" diameter) which is sealed with araldite on to the copper adapter at the end of the thermocouple tube (Fig. 5). The thermocouple is then inserted into a 0.1" diameter stainless steel tube, which is placed inside the crucible and silver brazed to its top as shown in Fig. 5. This arrangement ensures good thermal contact with the solvent bath and prevents any shift in the position of thermocouple. The free end of the thermocouple wires are then soldered to 20 gauge enameled copper wires using $ZnCl_2$ flux. These junctions are kept immersed in small pools of diffusion pump oil maintained in glass tubes. The glass tubes are kept in a Dewar flask packed with finely ground ice. The top of Dewar

flask is well insulated and protected from draught. The cold junction leads are connected to K₄ Leads & Northrup potentiometer (type 7554). The potentiometer is capable of reading 1.6 volts in units of 0.5 μ v. The potentiometer is connected to a Leads & Northrup galvanometer (type 2430) as null point detector. The potentiometer draws its power from a 2 volts Leads & Northrup constant voltage supply unit and is standardised against a standard cadmium cell. The sensitivity of the galvanometer is 0.5 μ v/mm. It is enough to permit the measurement of temperature difference upto 0.005°C. In order to reduce vibrations the galvanometer is mounted on the shock absorbing pads.

3.3. Procedure

Since the temperature of the calorimeter was about 200°C, the bismuth-tin eutectic of composition (47% wt. Sn and 53% wt. Bi) and melting temperature 147°C was selected. This solvent also does not react with stainless steel crucible. The eutectic alloy was prepared by melting bismuth and tin of 99.9% purity. About 650 gms of this alloy is loaded in to the crucible.

The loaded crucible is placed on the alumina supports along with the radiation shields. The thermocouple prepared in the manner already described is pushed down in the thermocouple stainless steel tube. The stainless steel stirrer is inserted in the stirrer tube through ball bearings and the wilson seal. The top flange assembly is cleaned with alcohol, greased and oiled at the required points e.g. gate valve, wilson seal and the addition tube etc. This assembly is rested on the mild steel flange of the lower steel shell. The system is evacuated and the water supply is switched on. In the beginning the power supply is kept low,

about 60 volts and 2.5 amps. As the temperature increases, the power supply is slowly increased to 125 volts and 5 amps. The stainless steel stirrer is pushed down till it touches the solid alloy in the crucible. As the alloy starts melting the stirrer is pushed down further. When the load is completely molten, the stirrer is pulled up about $1/4$ " above the bottom of crucible and attached to the driving mechanism by a rubber tube.

In the mean time the temperature is measured by the potentiometer. It takes about 10 hours to reach the melting point of the load and depending upon the temperature of operation it takes 4-6 hours for the load to melt. Usually it is left overnight so that the system reaches a steady state and a constant temperature is maintained.

Next morning the stirrer is started. The specimen is weighed and put into the glass addition tube. It is then evacuated through the ground glass valve. The glass addition tube is connected to the calorimeter by opening the gate valve. The addition tube containing the specimen is enclosed in a ice-water bath maintained in a Dewar flask. The cold junction is packed with finely ground ice. The potentiometer is standardised against standard cell and the mechanical zero of the galvanometer is adjusted. The temperature of the bath is noted as the function of time. When the temperature reaches a constant value the potentiometer and the galvanometer are again checked and the temperature is noted. The specimen is added by turning the specimen tube on the ground glass joint. The clock is started as the light spot on the galvanometer scale starts moving. Readings of the potentiometer are taken at fixed intervals of time for about 12 to 15 minutes. The readings are taken after every 15 seconds for first two minutes and then after intervals of 30 seconds. When the required

number of time-temperature readings have been taken, the gate valve is closed. The glass addition tube is disconnected from the ground glass joint. The metal bath is then allowed to come back to the equilibrium state before the next addition is made.

When required number of additions have been made, the power is slowly decreased first and then shut off. Before putting off the power supply the stirrer is pulled away from the molten bath. The furnace is then left to cool overnight. In the next morning the equipment is dismantled by a procedure opposite to one already described.

Chapter IV

RESULTS

4.1. Detail calculations for two additions

In the calorimetric experiment samples are added from a known temperature to a solvent bath of known weight and composition. The temperature change of the solvent with time is noted for each addition. The heat effect on dissolution of the added sample is calculated on the basis of time-temperature data. These calculations are illustrated for two additions.

A. Addition of a tungsten specimen (Table II, Exp. 2.1)

Solvent - 650 gms (47% wt. Sn and 53% wt. Bi)

Specimen - 1.7865 gms of tungsten (2 pieces) at 273°K

Since the heat content of tungsten is known and it does not dissolve in the solvent; this addition is used to calculate the heat capacity of the calorimeter.

In order to obtain the value of 'k' a plot of $\log (T_e - T)$ vs. t was made (Fig. 9). Using Eq. 3.1.14, the value of 'k' calculated from the slope of this graph was $10.73 \times 10^{-4} \text{ sec}^{-1}$.

The integral $\int_0^{300} (T_e - T)dt$ evaluated using the trapezoidal rule is 3143.7 $\mu\text{v-sec}$. Hence

$$k \int_0^{300} (T_e - T)dt = 10.73 \times 10^{-4} \times 3143.7 = 3.3839 \mu\text{v}$$

Time-Temperature Data for Exp. 2.1

<u>Time, 't', sec.</u>	<u>Temperature, T, °F</u>	<u>(T_e - T), °F</u>	<u>log (T_e - T)</u>
0	7511	-	-
15	7499.5	11.5	1.0607
30	7498.9	12.1	1.0828
45	7498.9	12.1	1.0828
60	7499.0	12.0	1.0792
75	7499.1	11.9	1.0755
90	7499.5	11.5	1.0607
105	7499.6	11.4	1.0569
120	7499.7	11.3	1.0531
150	7500.2	10.8	1.0334
180	7500.5	10.5	1.0212
210	7500.8	10.2	1.0086
240	7501.2	9.8	0.9912
270	7501.5	9.5	0.9777
300	7501.8	9.2	0.9638
330	7502.2	8.8	0.9445
360	7502.4	8.6	0.9345
390	7502.7	8.3	0.9191
420	7502.9	8.1	0.9085
450	7502.2	7.8	0.8921
480	7502.4	7.6	0.8808
510	7502.6	7.4	0.8692
540	7502.7	7.3	0.8633

$$\therefore \Delta T_{\text{corr.}} = \left[\Delta T_{\text{ob.}} + k \int_{t_0}^t \Delta T. dt \right] = 9.2 + 3.3839$$

$$= 12.5838 \text{ } \mu\text{v.}$$

Number of g-atoms of tungsten, $n_W = \frac{1.7865}{183.65} = 9.72 \times 10^{-3}$

From data in the literature⁽³⁹⁾ the heat content at $T_e = 7511 \text{ } \mu\text{v} \equiv 457.65^\circ\text{K}$ (Eq. 4.2.2) is

$$(H_{T_e} - H_{273.15})_W = 1103.6 \text{ cal/g-atom}$$

Hence the heat capacity of the calorimeter at the completion of the 1st addition is

$$C_{p_f} = \frac{n(H_{T_e} - H_{T_e \text{ sp.}})}{\Delta T_{\text{corr.}}}$$

$$= \frac{9.72 \times 10^{-3} \times 1103.6}{12.5838} = 0.8525 \text{ cal/ } \mu\text{v}$$

B. Addition of a lead specimen (Table II, Exp. 2.3)

Solvent - 650 gms of alloy (47% wt. Sn, 53% wt. Bi), 1.7865 gms of tungsten added in the first addition and 1.219 gms of bismuth added in the second addition.

Specimen - 1.17455 gms of lead (2 pieces) at 273°K

The heat effect on solution of lead in the bismuth-tin alloy is calculated in the following manner.

The value of k' is obtained from the slope of $\log(T_e - T)$ vs. t plot (Fig. 10) as $11.13 \times 10^{-4} \text{ sec}^{-1}$. At time $t = 240 \text{ sec.}$, $\Delta T_{\text{ob.}} = 13.4 \text{ } \mu\text{v.}$

Time-Temperature Data for Exp. 2.3

<u>Time, 't', sec.</u>	<u>Temperature, T, °F</u>	<u>(T_e - T), °F</u>	<u>log(T_e - T)</u>
0	7578.4	-	-
15	7561.0	17.4	1.2405
30	7561.6	16.8	1.2253
45	7562.2	16.2	1.2095
60	7562.3	16.1	1.2068
75	7562.5	15.9	1.2014
90	7562.6	15.8	1.1987
105	7562.6	15.8	1.1987
120	7562.8	15.6	1.1931
150	7563.3	15.1	1.1790
180	7564.0	14.4	1.1584
210	7564.5	13.9	1.1430
240	7565.0	13.4	1.1271
270	7565.5	12.9	1.1106
300	7566.0	12.4	1.0934
330	7566.4	12.0	1.0792
360	7566.6	11.8	1.0719
390	7567.0	11.4	1.0569
420	7567.3	11.1	1.0453
450	7567.8	10.6	1.0253
480	7568.1	10.3	1.0128
510	7568.5	9.9	0.9956

Contd. ...

Time, 't' sec.	Temperature, T, °K	$(T_e - T),$ °K	$\log(T_e - T)$
540	7568.9	9.5	0.9777
570	7569.1	9.3	0.9685
600	7569.5	8.9	0.9494
630	7569.8	8.6	0.9345
660	7570.1	8.3	0.9191
690	7570.3	8.1	0.9085
720	7570.5	7.9	0.8976
750	7570.7	7.7	0.8865

Using Eq. 3.1.14 and the trapezoidal rule

$$k \int_0^{340} \Delta T \cdot dt = 11.13 \times 10^{-4} \times 3556.0 = 3.957 \text{ } \mu\text{V}$$

$$\Delta T_{\text{corr.}} = 13.4 + 3.957 = 17.357 \text{ } \mu\text{V}$$

At $T_e = 459.36^\circ\text{K}$, the heat content (Eq. 4.2.1) is:

$$(H_{T_e} - H_{273.15})_{\text{Pb}} = 1207.15 \text{ cal/g-atom}$$

In order to obtain $C_{p_f}^{2.3}$ from the C_{p_f} value of Exp. 2.1, Eq. 3.1.15 is used.

Taking \bar{C}_p of the components lead and bismuth to be equal to the C_p of pure liquid components, we get

$$C_{p_f}^{2.3} = C_{p_f}^{2.1} + \frac{\bar{C}_{\text{PBi}} (n_{\text{Bi}}^{2.1} - n_{\text{Bi}}^{2.2}) + \bar{C}_{\text{PPb}} (n_{\text{Pb}}^{2.2} - n_{\text{Pb}}^{2.3})}{\theta}$$

where θ = thermoelectric power of the thermocouple used.

$$\therefore C_{p_f}^{2.3} = 0.8525 + \frac{7.6 \times 5.85 \times 10^{-3} + 7.1 \times 5.68 \times 10^{-3}}{40}$$

$$= 0.85465 \text{ cal/} \mu\text{V}$$

$$\therefore Q_{T_e} = \frac{0.85465 \times 17.357}{5.68 \times 10^{-3}} - 1207.15$$

$$= 1404 \text{ cal/g-atom.}$$

4.2. Evaluation of calorimetric data

Determination of heat of solution of lead in liquid Bi-Sn alloys

is made by measuring the heat effect on addition of a specimen of lead to Bi-Sn alloy solvent baths maintained in the calorimeter. The heat capacity of the calorimeter is found from the calibrating additions of tungsten or bismuth. The following equations of the heat contents of tungsten, lead and bismuth required for the calculations illustrated above have been taken from the literature⁽³⁹⁾.

$$\begin{aligned} \text{For lead} \quad (H_{T_e} - H_{273.15^\circ K})_{Pb(s)} &= C_{P_1} (T_e - 400) \\ &\quad + \frac{1}{2}(T_e + 400) \\ &\quad + 813.95 \text{ cal/g-atom} \quad 4.2.1 \end{aligned}$$

$$\begin{aligned} \text{For tungsten} \quad (H_{T_e} - H_{273.15^\circ K})_{W(s)} &= C_{P_1} (T_e - 400) \\ &\quad + \frac{1}{2}(T_e + 400) \\ &\quad + 756.8 \text{ cal/g-atom} \quad 4.2.2 \end{aligned}$$

$$\begin{aligned} \text{For bismuth} \quad (H_{T_e} - H_{273.15^\circ K})_{Bi(s)} &= C_{P_1} (T_e - 450) \\ &\quad + \frac{1}{2}(T_e + 450) \\ &\quad + 1125.3 \text{ cal/g-atom} \quad 4.2.3a \end{aligned}$$

$$\begin{aligned} H_{(fusion)_{T_e}} &= 2600 + (T_e - 544.5) \\ &\quad \left[7.6 - C_{P_1} \frac{1}{2}(T_e + 544.5) \right] \text{ cal/g-atom.} \quad 4.2.3b \end{aligned}$$

In these equations the subscript of C_p stands for the temperature at which the heat capacity is to be taken. The heat capacity data are taken from tables in ref. 39.

Usually in an experiment a number of additions are made to a particular load of metal in the crucible and the calculations are made in the manner described before. To calculate C_{Pf} for a particular addition from the previous calibrating additions, Eq. 3.1.18 is used. The partial gram-atomic heat capacities of lead and bismuth are taken as the heat capacity of liquid lead and bismuth of solution temperature.

The results of various additions are listed in Table II. In the experiments no. 1, 2 and 3 tungsten is used as the calibrating addition. In experiments no. 1 and 2 bismuth additions have been made and the heat effect on solution of bismuth in the 40 at.% Bi-Sn alloy has been calculated (Table II). From the heat effect on solution of bismuth (Table II), the partial gram-atomic enthalpy of bismuth relative to liquid bismuth is calculated as 41.4 and 51.8 cal/g-atom at 464.75°K (Exp. 1.4) and 459.15°K (Exp. 2.2) respectively. The average value is 46.7 cal/g-atom for $\Delta \bar{H}_{Bi(l)}$ in 40 at. % Bi-Sn alloys at 462°K. The only reported value⁽³⁹⁾ of $\Delta \bar{H}_{Bi(l)}$ in 40 at. % Bi-Sn alloys is 30 cal/g-atom at 608.1°K and it is in good agreement with our value. The value reported in the literature is not expected to be accurate as it is based on e.m.f. data. The heat capacity of the calorimeter (C_{Pf}) for the experiment no. 4 is calculated from the bismuth calibrating additions. The heat effect on addition of bismuth is calculated by the following equation which is based on $\Delta \bar{H}_{Bi(l)}$ calculated above.

$$\text{Total heat effect } \Delta H_T = 3772.0 + C_{Pf} (T_e - 450) + \frac{1}{2}(T_e + 450)$$

$$+ (T_e - 544.5) \times 0.9$$

4.2.4

Summary of data and results of experiments involving additions of lead, bismuth and tungsten to molten bismuth-tin bath containing 40 at. % Bi (53% wt. Bi)

Exp. No.	Type	Addition No. of g-atom added from 3 273°K. $\times 10^3$	T_e °K	$\Delta T_{ob.}$, μV	$k \times 10^4$, sec^{-1}	$\Delta T_{corr.}$, μV	C_p , $cal/\mu V$	$Q_{T_e} [\frac{1}{T_e} \rightarrow \frac{1}{T_e}]$ $cal/g-atom$
1.1	W	11.7	465.1	12.0	11.82	16.83	0.7985	-
1.2	Pb	6.19	465.1	15.7	7.122	20.5618	0.79963	1410.0
1.3	Pb	5.68	464.65	13.9	7.43	18.6109	0.80067	1381.0
1.4	Bi	4.55	464.75	13.9	14.12	21.525	0.80154	2570.0
1.5	Pb	5.63	464.05	14.2	10.05	18.346	0.80298	1378.0
1.6	Pb	4.063	464.0	9.6	7.95	13.250	0.80375	1383.0
2.1**	W	9.72	457.65	9.2	10.73	12.5838	0.8525	-
2.2	Bi	5.84	459.15	18.6	7.58	25.72	0.8536	2575.0
2.3	Pb	5.68	459.35	13.4	11.131	17.357	0.85465	1404.0
2.4	Pb	6.07	459.45	15.2	10.6	18.565	0.85576	1413.0
2.5	Pb	3.67	459.85	6.25	15.35	11.1672	0.85564	1395.0
3.1	W	11.41	468.75	11.5	7.00	13.305	1.0043	-
3.2	Pb	6.305	461.30	14.6	6.0	16.40	1.00644	1397.0
3.3	Pb	6.01	460.59	9.1	10.72	15.43	1.00754	1371.0
3.4	Pb	5.7	460.27	8.2	10.6	14.534	1.0086	1358.0
4.2	Pb	5.57	465.85	13.1	11.42	16.3478	0.8742	1314.0
4.1	Bi	4.45	466.4	17.4	7.43	19.415	0.8732***	-
4.3	Pb	4.57	465.09	9.8	14.8	14.21	0.87509	1374.0
4.4	Pb	4.365	464.65	7.7	16.51	12.971	0.87709	1365.0
4.5	Pb	4.525	463.80	7.55	14.7	13.448	0.88050	1380.0
4.6	Pb	4.408	463.09	7.3	11.71	13.2454	0.88131	1416.0

* No. 2.4 indicates addition no. 4 in experiment No. 2.
 ** Some amount of lead was already present in the bath before the start of experiment.
 *** See text for details.

4.3. Partial gram-atomic enthalpy of lead in 40 at. % Bi-Sn alloys

The partial gram-atomic enthalpy of lead in liquid bismuth-tin alloys is equal to the heat effect on dissolution of lead in the bath corresponding the average composition of the bath before and after the addition⁽³¹⁾.

$$Q_{i,T_e} = \Delta \bar{H}_{i,T_e} X_i \quad 4.3.1$$

where

$$X_i = \frac{1}{2} \left(\frac{n_i^0}{n_i^0 + n_j^0 + n_k^0} + \frac{n_i^0 + n_i}{n_i^0 + n_i + n_j^0 + n_k^0} \right) \quad 4.3.2$$

n_i^0 , n_j^0 , n_k^0 are the number of g-atom of lead, tin and bismuth in the bath before the addition and n_i is number of g-atom of lead addition.

The values of $\Delta \bar{H}_{Pb(s)}$ i.e. the partial gram-atomic enthalpy relative to solid lead are listed in Table III along with X_{Pb} . These values correspond to an average temperature of $462 \pm 2^\circ K$.

For the analysis of these results it is necessary to know the partial gram-atomic enthalpy relative to liquid lead. These values can be calculated by subtracting heat of fusion of lead at T_e °K from the values of $\Delta \bar{H}_{Pb(s)}$. The heat of fusion of lead is evaluated by the following equation formulated on the basis of data in literature⁽³⁹⁾.

For lead. $\Delta H_{(fusion), T_e} = 1140 + 0.47 (T_e - 600.6) \text{ cal/g-atom}$ 4.3.3

$\Delta \bar{H}_{Pb(l)}$ values obtained are listed in Table III. The values of $\Delta \bar{H}_{Pb(s)}$ and $\Delta \bar{H}_{Pb(l)}$ are plotted against X_{Pb} in Figs. 11 and 12 respectively and the best fitting statistical lines have been drawn. The equation for

Table III

Experimental values of $\Delta \bar{H}_{\text{Pb(s)}}$ and $\Delta \bar{H}_{\text{Pb(l)}}$ as functions of X_{Pb} in a solvent with $X_{\text{Sn}}/X_{\text{Bi}} = 1.5$ at 462°K.

Exp. No.	$X_{\text{Pb}} \cdot 10^3$	$\Delta \bar{H}_{\text{Pb(s)}}, \text{ cal/g-atom}$	$\Delta \bar{H}_{\text{Pb(l)}}, \text{ cal/g-atom}$
1.2	0.768	1410	206
1.3	2.238	1381	177
1.5	4.8752	1378	174
1.6	6.07	1383	179
2.3	7.2403	1404	198
2.4	8.626	1413	207
2.5	9.7743	1395	189
3.2	1.8435	1397	192
3.3	3.164	1371	165
3.4	4.418	1358	152
4.2	0.639	1314	111
4.3	1.801	1374	170
4.4	2.824	1365	161
4.5	6.103	1380	176
4.6	7.119	1416	211

these lines are:

$$\Delta \bar{H}_{\text{Pb(s)}} = 1364 + 4.175 \times 10^3 X_{\text{Pb}}, \text{ cal/g-atom, } X_{\text{Pb}} < 0.010 \quad 4.3.4$$

$$\Delta \bar{H}_{\text{Pb(l)}} = 160 + 4.13 \times 10^3 X_{\text{Pb}}, \text{ cal/g-atom, } X_{\text{Pb}} < 0.010 \quad 4.3.5$$

The mean scatter of points as given by root mean square deviation is ± 20 cal/g-atom. The partial gram-atomic enthalpy of lead in the 40 at. % Bi-Sn alloy at infinite dilution is 1364 ± 20 cal/g-atom relative to solid lead at 462°K.

Chapter V

DISCUSSION

5.1. Discussion of errors

The errors in the reported values can be separated into two categories.

1. Random errors
2. Systematic errors

Inspection of Eqs. 3.1.14, 3.1.16 and 3.1.17 shows that the random errors arise from uncertainties in the values of the temperature of the solvent bath (T_e), $\Delta T_{\text{corr.}}$, initial temperature of specimen T_0 , the weight of the specimen and the estimated value of C_{pf} for non-calibrating additions. Uncertainty in the measurement of temperature is $\pm 0.0025^\circ\text{C}$. Thus uncertainty in $\Delta T_{\text{ob.}}$ is $\pm 0.5\%$. Errors in $\Delta T_{\text{corr.}}$ depend upon the uncertainties in $\Delta T_{\text{ob.}}$ and $k \int_{t_0}^t \Delta T_{\text{ob.}} dt$. The scatter in the plot of $\log \Delta T$ against 't' gives the error in $k \int_{t_0}^t \Delta T_{\text{ob.}} dt$ of about $\pm 1\%$. Since $k \int_{t_0}^t \Delta T_{\text{ob.}} dt$ is about one fourth of $\Delta T_{\text{corr.}}$, the total error in $\Delta T_{\text{corr.}}$ is $\pm 0.6\%$. It is found that the scatter in the plot of $\log \Delta T$ against 't' is large at higher time. Therefore $\Delta T_{\text{corr.}}$ is always calculated taking $\Delta T_{\text{ob.}}$ at a lower time. The uncertainty in $\Delta T_{\text{corr.}}$ is greater than the uncertainty introduced in it through uncertainty in potential measurement (0.5%). This difference arises from oxidation effects, time lag in the measuring unit, thermal and compositional non-uniformity etc.

The uncertainty in the weight of specimen is 0.005%. The equilibrium temperature (T_0) is taken as the temperature at zero time. The uncertainty of $\pm 0.005^\circ\text{C}$ in T_0 gives rise to negligible uncertainty in the heat content values. The uncertainty in the estimated C_{P_f} value arises from the uncertainty in $\Delta T_{\text{corr.}}$ and is $\pm 0.6\%$. Thus the total random error should be under 1.2%. This error is reflected in the scatter we get in the results of the partial gram-atomic enthalpy of lead. The total heat effect of lead additions is about 2600 cal/g-atom. Therefore, the scatter is expected to be less than ± 35 cal/g-atom. The root mean square scatter in the measured values of partial gram-atomic enthalpy relative to solid lead is ± 20 cal/g-atom.

Systematic errors arise from the uncertainty in the reported values of heat capacity for tungsten, lead and bismuth. The systematic errors in the heat capacity of tungsten will introduce systematic errors in C_{P_f} which in turn will introduce error in $\Delta \bar{H}_{\text{Pb}}$. Again errors in the heat capacity of lead will also introduce errors in the values of $\Delta \bar{H}_{\text{Pb}}$. The systematic error in the calculation of $\Delta \bar{H}_{\text{Pb}(l)}$ will be greater than this value because of uncertainty in the heat of fusion of lead. The experiment calibrated by the bismuth additions will contribute a systematic error due to the uncertainty in the heat effect on dissolution of bismuth. However, the exact magnitude of systematic errors can not be calculated as the uncertainty in the heat capacity values are not available⁽³⁹⁾.

5.2. Performance of calorimeter

As pointed out in section 2.3, the performance of the calorimeter is determined primarily by two criteria. The present calorimeter satisfies these two conditions.

- (i) The temperature of environment is stable to $\pm 0.005^\circ\text{C}$ throughout a reaction. This is an essential feature of a solution calorimeter as the basic heat transfer law depends upon this assumption.
- (ii) The calorimeter is so constructed that heat transfer takes place mainly by radiation. This deduction can be made by comparing the experimental heat transfer coefficient with that calculated theoretically for heat transfer by radiation.

From Eqs. 3.1.4 and 3.1.13

$$k = \frac{K}{C_{p_f}} = \frac{4\pi^3 K_R}{C_{p_f}} \quad 5.2.1$$

where $K_R = \frac{\sigma S E}{J}$

E = emissivity, 0.2 for polished metals

C_{p_f} = heat capacity of the calorimeter

S = surface area

σ = Stefan's constant, 5.67×10^{-5} ergs $\text{cm}^{-2} \text{sec}^{-1} \text{degree}^{-4}$.

J = 4.2×10^7 ergs/cal.

Substituting 460°K for T_e , 32 cal/deg. for C_{p_f} and the average surface area of the inner most radiation shield and the crucible, 250 cm^2 for S , we get,

$$k = 8.25 \times 10^{-4} \text{ sec}^{-1}$$

Thus the theoretically calculated value of 'k' is in good agreement with the value of $10 \pm 2.5 \times 10^{-4} \text{ sec}^{-1}$ obtained experimentally.

Further deduction can be made by comparing the heat capacity of the calorimeter with that calculated theoretically from the known weight of the alloy in the crucible. The values of heat capacities determined experimentally are listed in Table IV along with the values of the heat capacities calculated theoretically. The theoretically calculated values are less than the experimental values. This discrepancy arises because of the contributions to the final heat capacity by the stainless steel crucible, the stirrer rod, the supports and conduction effects. However, the measured heat capacities monotonically increase with increase in the calculated heat capacities.

The performance of this calorimeter may be compared with those of the other calorimeters from the data compiled in Table V. It is obvious from Table V that this calorimeter compares favourably with other calorimeters. However, there are certain limitations. The operating temperature and the sensitivity of temperature measuring unit are rather low and the vacuum is not sufficiently high. It is also desirable to improve the temperature stability of the environment. These limitations of this calorimeter can be overcome by the use of sophisticated equipments which are not available at present. For low operating temperatures used in these experiments, the vacuum of 2.5×10^{-2} mm of Hg is found to be satisfactory. However, high vacuum is required to avoid oxidation of liquid metal bath and further reduce the heat transfer coefficient at higher working temperatures.

Table IV

Comparison of the measured heat capacities of the calorimeter
with those calculated theoretically.

Exp. No.	Theoretically calculated C_{p_f} , cal/g-atom/°K	Measured value of C_{p_f} , cal/g-atom/°K	Difference
1.1	29.421	31.940	2.519
2.1	31.107	34.100	2.993
4.1	31.514	34.925	3.414
3.1	33.920	40.147	6.227

Table V
Comparison of present calorimeter with other calorimeters.

Details	This calorimeter	Other calorimeters
1. The thermostat	Metal block	Salt ^(15,16) bath and metal block ^(12,18)
2. Temperature range	150° - 200°C	250° - 500°C
3. Temperature control	On-off controller ± 0.005°C	Electronic ^(15,16) or on-off ^(12,18) controller ± 0.010° - 0.001°C
4. Calorimetric unit	Stainless steel crucible of thickness 0.05"	Dewar flask ⁽¹⁵⁾ , Mo-crucible ⁽¹⁶⁾ or graphite crucible ⁽¹²⁾
5. Stirrer	Stainless steel rod, 0.1" diameter	Glass stirrer ⁽¹⁵⁾ , Mo-stirrer ^(16,18) or graphite stirrer ⁽¹²⁾
6. Sensitivity of the temperature measuring unit	0.005°C	0.005° - 0.001°C
7. Calibration	Chemical (W)	Chemical (W, Sn) ^(15,16,18) or electrical ⁽¹²⁾
8. Environment	Vacuum, 2-5 x 10 ⁻² mm of Hg	Vacuum, 10 ⁻³ to 10 ⁻⁴ mm of Hg or Argon gas
9. Accuracy of measurements	± 0.8%	± 0.2 - 2%
10. Plot of log ΔT vs. t	Linear over the entire range	In some cases ^(15,16) linear over the entire range while in others ^(12,18) non-linear

5.3. Constitution of the dilute bismuth-tin-lead solutions

Values for the partial gram-atomic enthalpy of lead in the bismuth-tin-lead ternary system have not yet been reported in the literature. The values measured in this investigation may be compared with the values predicted by the statistical models of dilute solutions such as regular solution model and the quasi-chemical theory. Also this analysis will throw some light on the constitution of these solutions.

In the regular solution model it is assumed that the solution is random and the co-ordination number Z and the bond energy ϵ are independent of composition. The relative partial gram-atomic enthalpy and its composition dependence are given by following equations derived by Jena⁽⁴⁰⁾:

$$\Delta \bar{H}_{k,m, x_k \rightarrow 0}^T = -(N Z W_{ij}) X_i X_j + (N Z W_{jk}) X_j + (N Z W_{ik}) X_i \quad 5.3.1$$

and

$$\left(\frac{d \Delta \bar{H}_k^T}{d X_k} \right)_{m, x_k \rightarrow 0} = 2(N Z W_{ij}) X_i X_j - 2(N Z W_{jk}) X_j - 2(N Z W_{ik}) X_i \quad 5.3.2$$

where $\Delta \bar{H}^T$ = the partial gram-atomic enthalpy given by regular solution model

m = ratio of atom fraction of two components, (X_i/X_j)

N = Avogadro's number

$$W_{ij} = \epsilon_{ij} - \frac{1}{2} \epsilon_{ii} - \frac{1}{2} \epsilon_{jj}$$

i, j and k stand for bismuth, tin and lead respectively and the superscript o stands for their pure state. For the evaluation of these equations, the values of $N Z W_{\text{Sn-Pb}}$ and $N Z W_{\text{Bi-Pb}}$ at 462°K are taken as $+1350^{(12)}$ and $-860^{(39)}$ cal/g-atom respectively. The bismuth-tin system behaves in a simple manner⁽³⁹⁾ with a ΔH value of only about 25 cal/g-atom at equi-atomic composition at 608°K . Therefore the regular solution model is applied to the value of 47 cal/g-atom obtained for $\Delta \bar{H}_{\text{Bi}(1)}, x_{\text{Bi}} = 0.4$ at 462°K and a value of 128 cal/g-atom is calculated for $N Z W_{\text{Sn-Bi}}$. The values of $\Delta \bar{H}_{\text{Pb}(1)}^T$ at infinite dilution and its composition dependence obtained from Eqs. 5.3.1 and 5.3.2 are 435 and - 870 cal/g-atom respectively. The calculated value of $\Delta \bar{H}_{\text{Pb}(1)}, x_{\text{Pb}} \rightarrow 0$ is higher than the measured value of 160 cal/g-atom. The measured value of the composition dependence of partial g- atomic enthalpy at infinite dilution is 4130 cal/g-atom and it differs appreciably from the calculated value of - 870 cal/g-atom.

The negative deviation of the experimental value suggests that the number of Bi-Pb bonds in solution is larger than that predicted by the regular solution model. The non-randomness of the dilute bismuth-tin-lead solution can be taken into consideration by using the quasi-chemical theory. This theory assumes that the co-ordination number Z and the bond energy ϵ are independent of composition but the number of various type of bonds N_{ij} is determined by the energy of bonds. The relative partial gram-atomic enthalpy of an element k in the dilute solution of a non-random ternary alloy i - j - k and the composition dependence of the partial gram-atomic enthalpy can be obtained from the expression derived by Jena⁽⁴⁰⁾.

$$\Delta \bar{H}_{k,m}, X_k \rightarrow 0 = \Delta \bar{H}_{k,m}^r, X_k \rightarrow 0 + \sum N Z W_{ij} \frac{d(\frac{\alpha_{ij}}{Z})}{d X_k} + (\frac{\alpha_{ii}}{Z})_{X_k \rightarrow 0} \quad 5.3.3$$

$$\left(\frac{d \Delta \bar{H}_k}{d X_k} \right)_{m, X_k \rightarrow 0} = \left(\frac{d \Delta \bar{H}_k^r}{d X_k} \right)_{m, X_k \rightarrow 0} + \sum N Z W_{ij} \frac{d^2 (\frac{\alpha_{ij}}{Z})}{d X_k^2} \quad 5.3.4$$

where the summation is taken over ij , jk and ik . The co-efficient α_{ij} accounts for the departure from randomness. Expressions for α_{ij} are given in ref. 40 in terms of X_1 , X_j , X_k , $N Z W_{ij}$, $N Z W_{jk}$, $N Z W_{ik}$ and Z . In order to evaluate these equations the co-ordination number Z in the dilute solution of lead in bismuth-tin alloys must be known. The value of Z , obtained for a liquid alloy from diffraction data, depends upon the method of obtaining the area under the first peak of the radial distribution curve. (37,41) When the diffraction data are evaluated by the same method, a value of 7.6 is obtained for both bismuth (41) and tin (37). With this value of Z Eqs. 5.3.3 and 5.3.4 are evaluated.

Equation 5.3.3 yields a value of 260 cal/g-atom for $\Delta \bar{H}_{Pb(1)}$, $X_{Pb} \rightarrow 0$ which compares reasonably with the measured value of 160 cal/g-atom.

However, the value of - 265 cal/g-atom for the composition dependence of $\Delta \bar{H}_{Pb(1)}$ evaluated from Eq. 5.3.4 is not much different from that predicted by the regular solution model.

The quasi-chemical theory assumes that the bond energies are

independent of composition. In the dilute solution of lead in bismuth-tin alloys, lead atoms are in an environment different from that in pure liquid lead. Therefore, the relative energy of Pb-Pb bonds $\Delta \epsilon_{\text{Pb-Pb}}$ may be expected to have a non-zero value. The required modifications in the quasi-chemical theory have been made by Jena⁽⁴⁰⁾ to take this non-zero value of $\Delta \epsilon_{\text{Pb-Pb}}$ into account. Using his equations a value of $\frac{1}{2} N Z \Delta \epsilon_{\text{Pb-Pb}}$ can be calculated from the experimental value of the composition dependence of $\Delta \bar{H}_{\text{Pb}(1)}$. This value is 2030 cal/g-atom. Thus a change of about 4.35% in the bond energy (relative to the heat of vapourisation of lead of 46.6 kcal/g-atom.⁽³⁹⁾) can account for the observed discrepancy in measured value. Jena et. al.⁽³²⁾ has shown that the change in bond energy has only a negligible effect on the relative partial gram-atomic enthalpy at infinite dilution.

It may be noted that similar analysis performed for other systems⁽⁴²⁾ also show change in bond energy of about 2-10%. As reported by Jena et. al.⁽³²⁾, in the dilute solution of gold in the bismuth-tin alloys, the calculated composition dependence of partial gram-atomic enthalpy differs appreciably from the measured value. A change of about 6% in the bond energy of Au-Au bonds accounts for this difference. However, the measured partial enthalpies at infinite dilution of gold in bismuth-tin alloys differ by about 700 cal/g-atom. This difference is suggested to be due to the difference of co-ordination number Z of gold in solution from that in the solvent. In bismuth-tin-lead system the co-ordination number Z is unlikely to be different, because the atomic volumes of elements bismuth and tin are nearly same as that of lead.^(36,37) Therefore, the experimentally and theoretically calculated values are not expected to be much different. In fact, the measured value of the partial gram-atomic

enthalpy of lead at infinite dilution in the bismuth-tin alloys is only about 100 cal/g-atom less than that predicted by the quasi-chemical theory.

The quasi-chemical theory neglects the vibrational entropy. However, any effect of vibrational entropy is likely to be small because of the small $\Delta \bar{H}$ values and low temperatures. It may be concluded that the discrepancy between the measured value of composition dependence of partial gram-atomic enthalpy and the value calculated by quasi-chemical theory is mainly due to the change in the energy of Pb-Pb bonds.

5.4. Conclusion

- I A liquid metal solution calorimeter has been designed and fabricated. Its performance compares well with other liquid metal solution calorimeters. Some of its salient features are following:
 - (i) The temperature control of the calorimeter is $\pm 0.005^\circ\text{C}$.
 - (ii) Precision of temperature measurement is 0.005°C .
 - (iii) The value of the heat transfer coefficient is found to be independent of time.
 - (iv) The overall precision of measurement of heat of solution is $\pm 0.8\%$.
- II The partial gram-atomic enthalpy of bismuth in 40 at. % Bi-Sn alloys relative to liquid bismuth is found to be 47 cal/g-atom at 462°K .
- III The partial gram-atomic enthalpy of lead in 40 at. % Bi-Sn alloys relative to solid lead at infinite dilution has been measured as 1364 ± 20 cal/g-atom at 462°K .
- IV The composition dependence of partial gram-atomic enthalpy of lead relative to liquid lead at infinite dilution is 4130 cal/g-atom

V It is found that the measured values of the partial gram-atomic enthalpy of lead at infinite dilution and its composition dependence deviate considerably from those calculated on the basis of regular solution model. However, the measured value of partial gram-atomic enthalpy is in good agreement with the value calculated from the quasi-chemical theory. The discrepancy between the measured value of composition dependence of partial gram-atomic enthalpy and the value calculated from the quasi-chemical theory is mainly due to the change in the energy of Pb-Pb bonds.

5.5. Suggestions for further work

I Calorimeter: The scope of this calorimeter and accuracy of measurement can be improved by following modifications:

1. The calorimeter has been designed to operate upto 400°C but as such only half of this range can be used. The temperature range can be increased by improving insulations and heating coils.
2. The vacuum in the calorimeter can be improved to $10^{-3} - 10^{-4}$ mm of Hg by the use of large capacity diffusion pump. This will reduce the 'k' value to half of its present value.
3. The sensitivity of the temperature measurement can be improved by the use of galvanometer-amplifier.
4. The use of constant voltage supply unit and air-conditioner will certainly improve temperature control of the calorimeter.
5. An automatic temperature recorder of high precision and speed will be a great asset with this calorimeter. Unfortunately this machine is very expensive.

II Bismuth-tin-lead system: It would certainly prove interesting to measure the partial gram-atomic enthalpy of lead in the bismuth-tin alloys over a range of composition of solvent bath and temperature. It would help in better understanding of the thermodynamic behavior of this system.

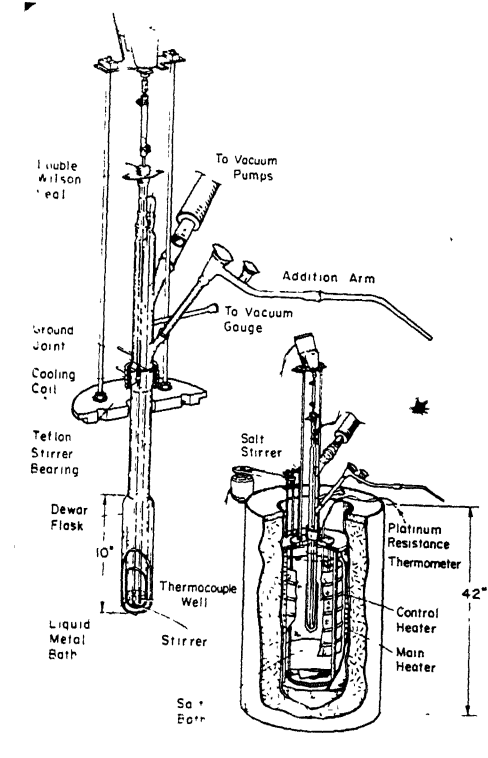


Fig. 1. Bever's Calorimeter.

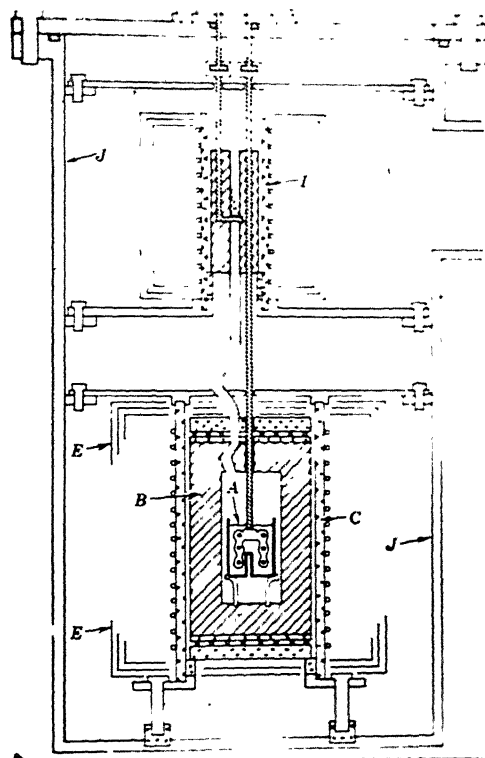


Fig. 2. Hultgren's Calorimeter. A, liquid tin bath; B, metal block; C, alumina tube supporting furnace winding; E, radiation shields; I, sample heating furnace; J, vacuum jacket.

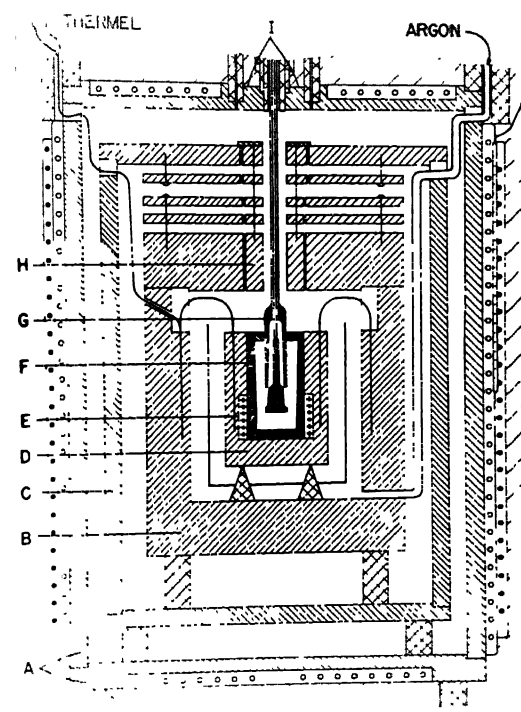


Fig. 3. Kleppa's Calorimeter. A, furnace core with heaters; B, constant temperature jacket; C, heavy shields; D, calorimeter block; E, calibration heater; F, removable crucible; G, charging and stirring device; H, inner plug; I, part of outer plug.

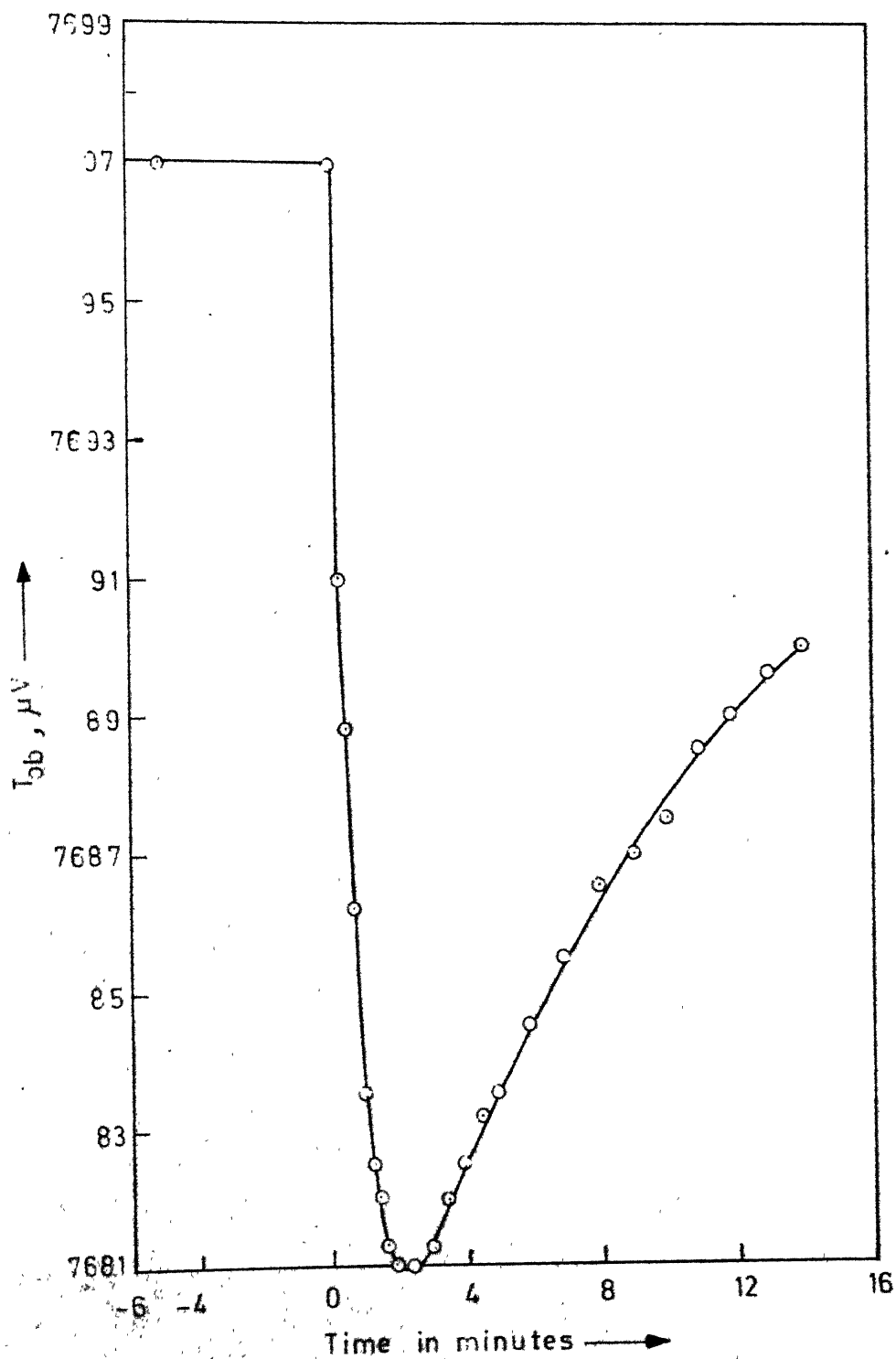
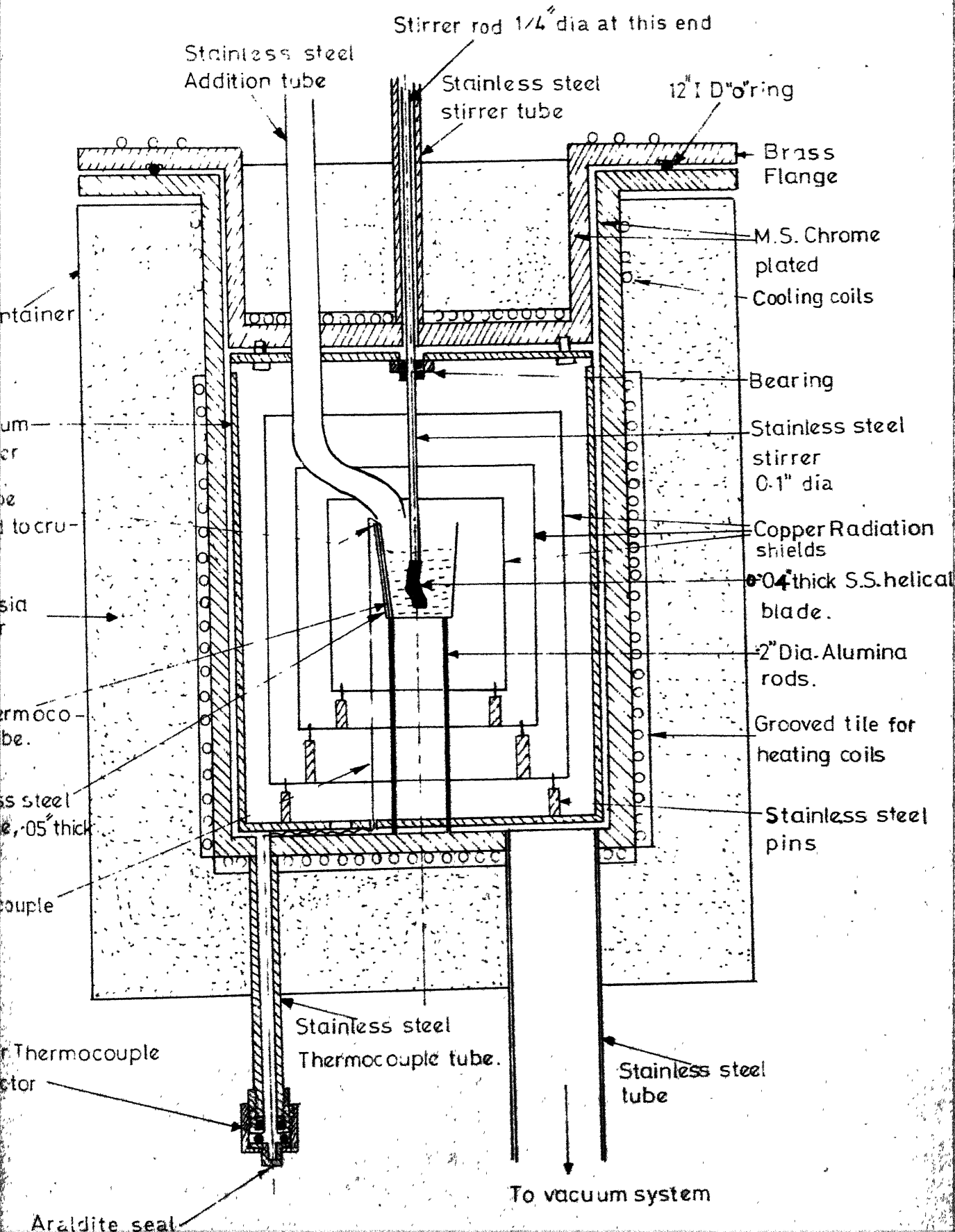
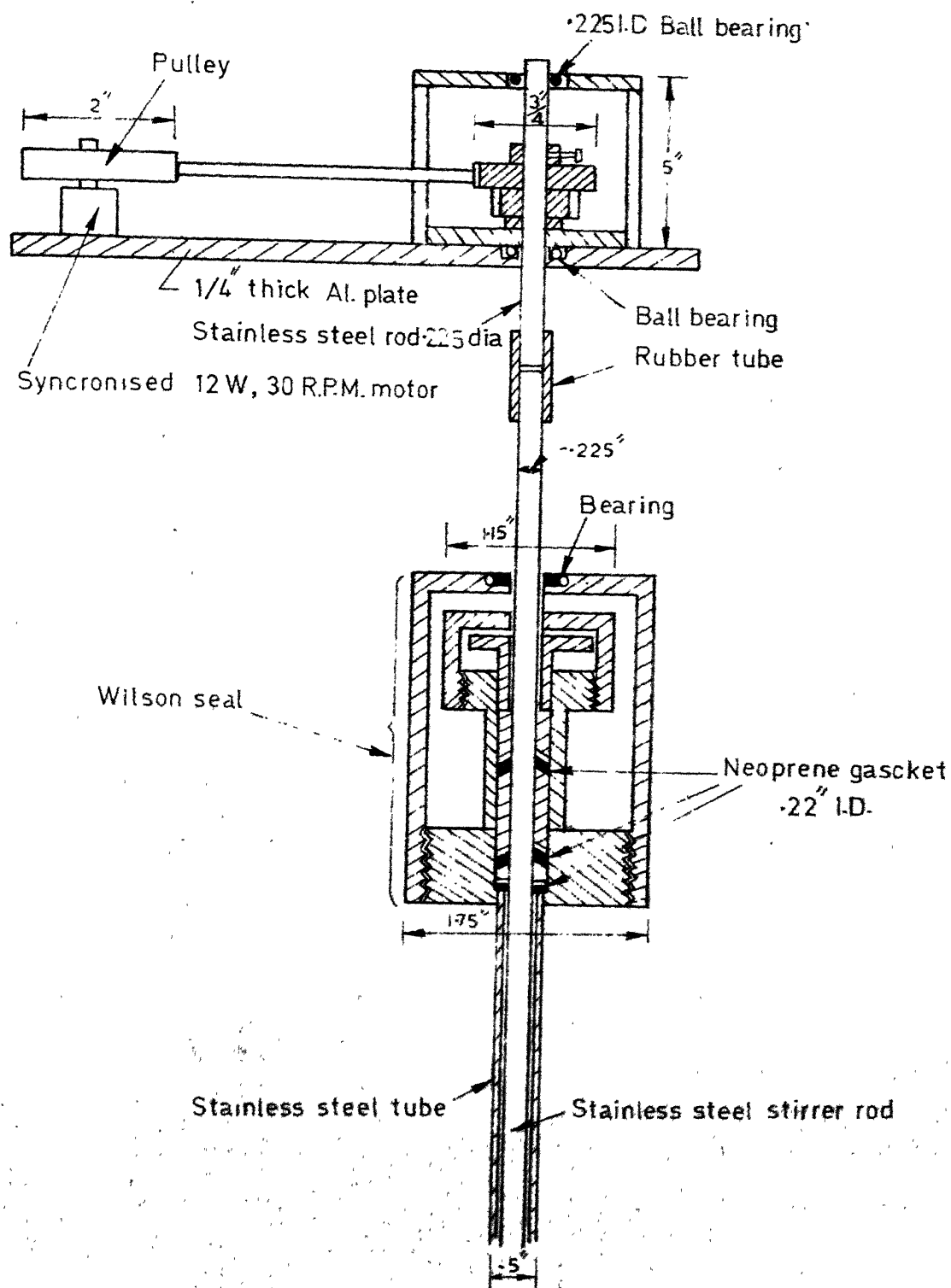
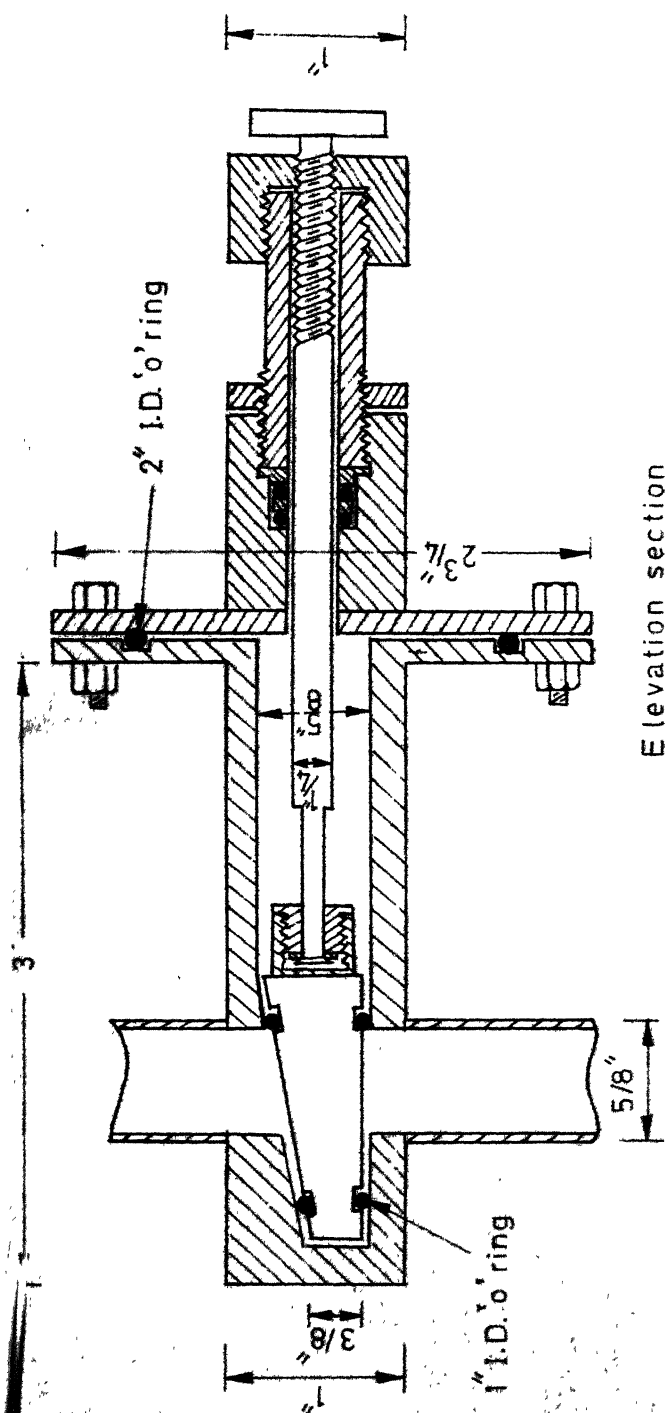


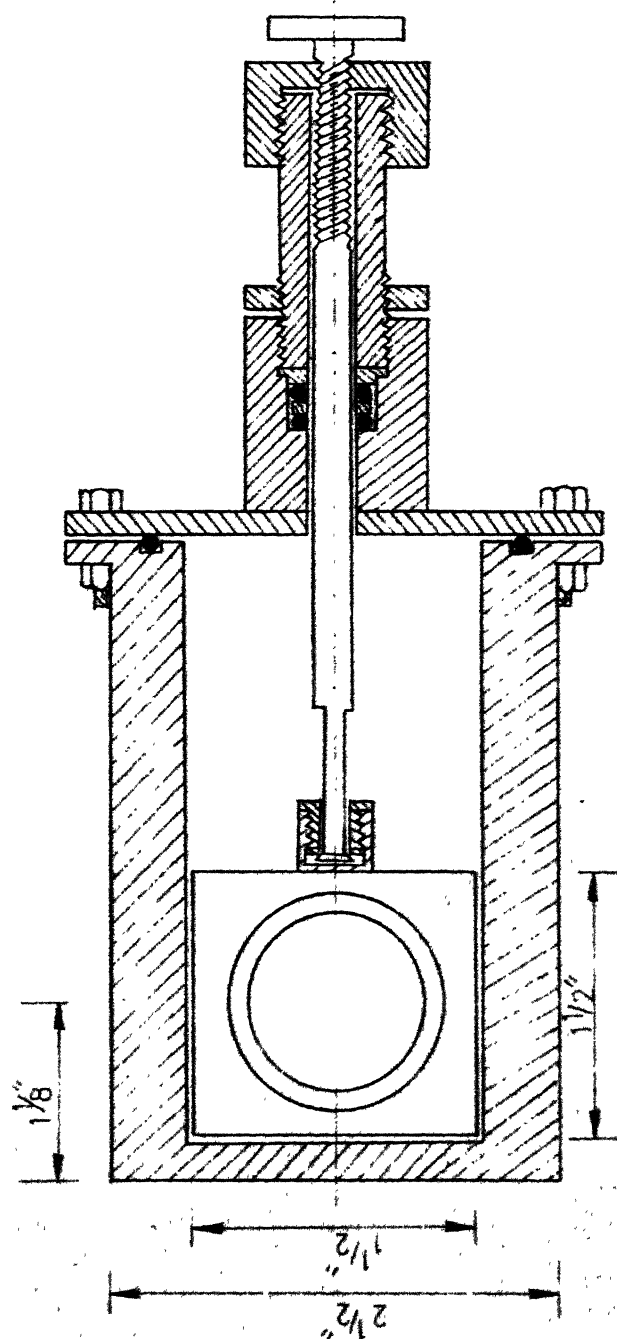
Fig. 4. Plot of T_{ob} against time for an addition.



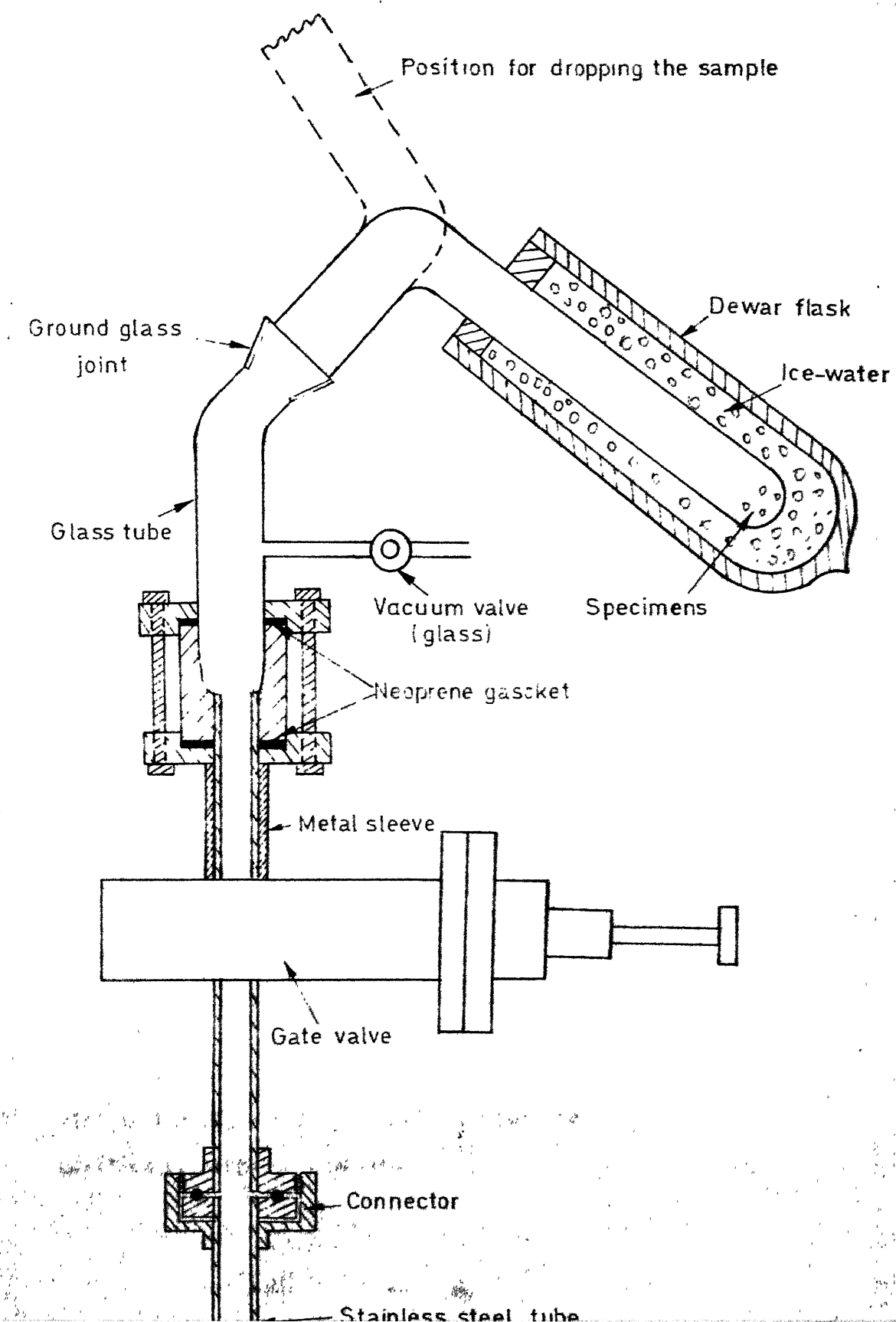




Elevation section



Elevation section



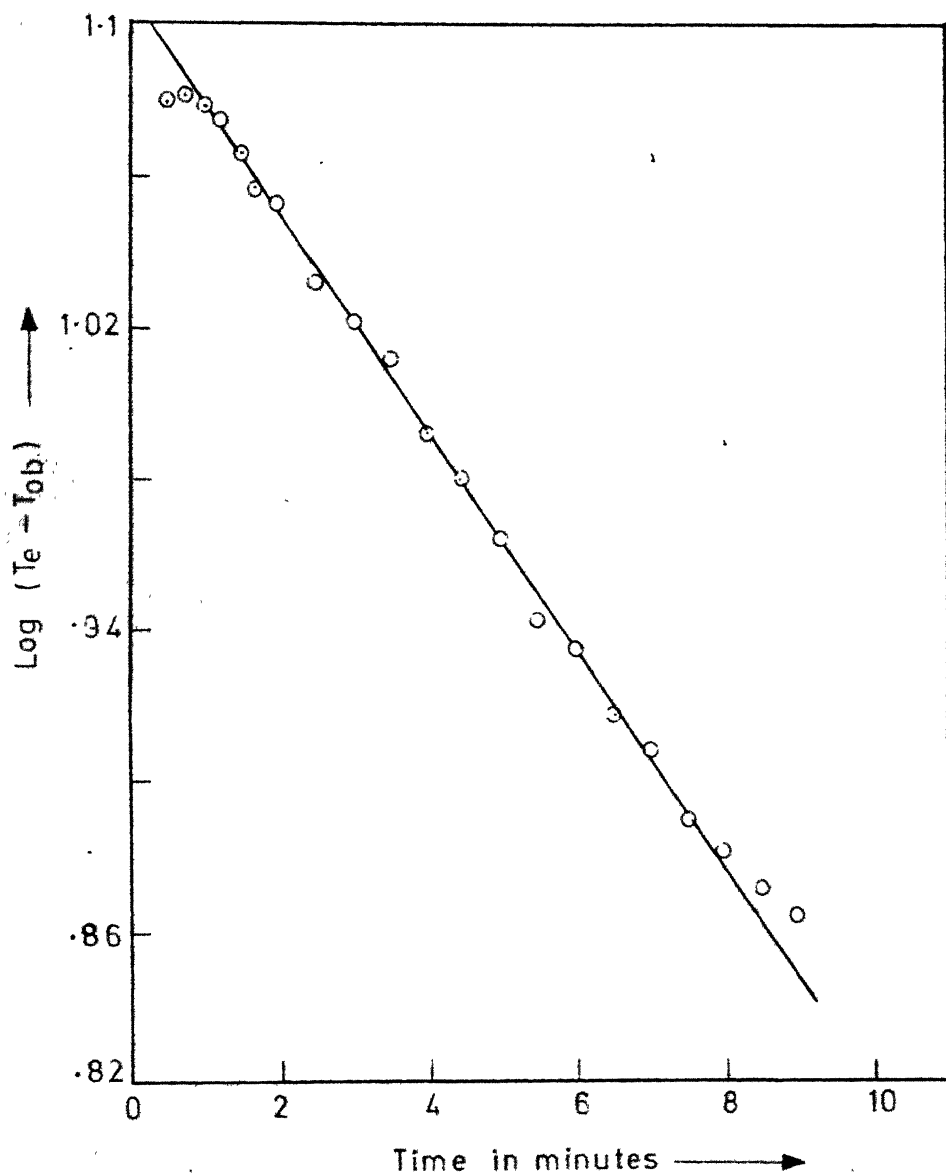


Fig. 9. Plot of $\log (T_e - T_{ob})$ against time for the addition of tungsten specimen.

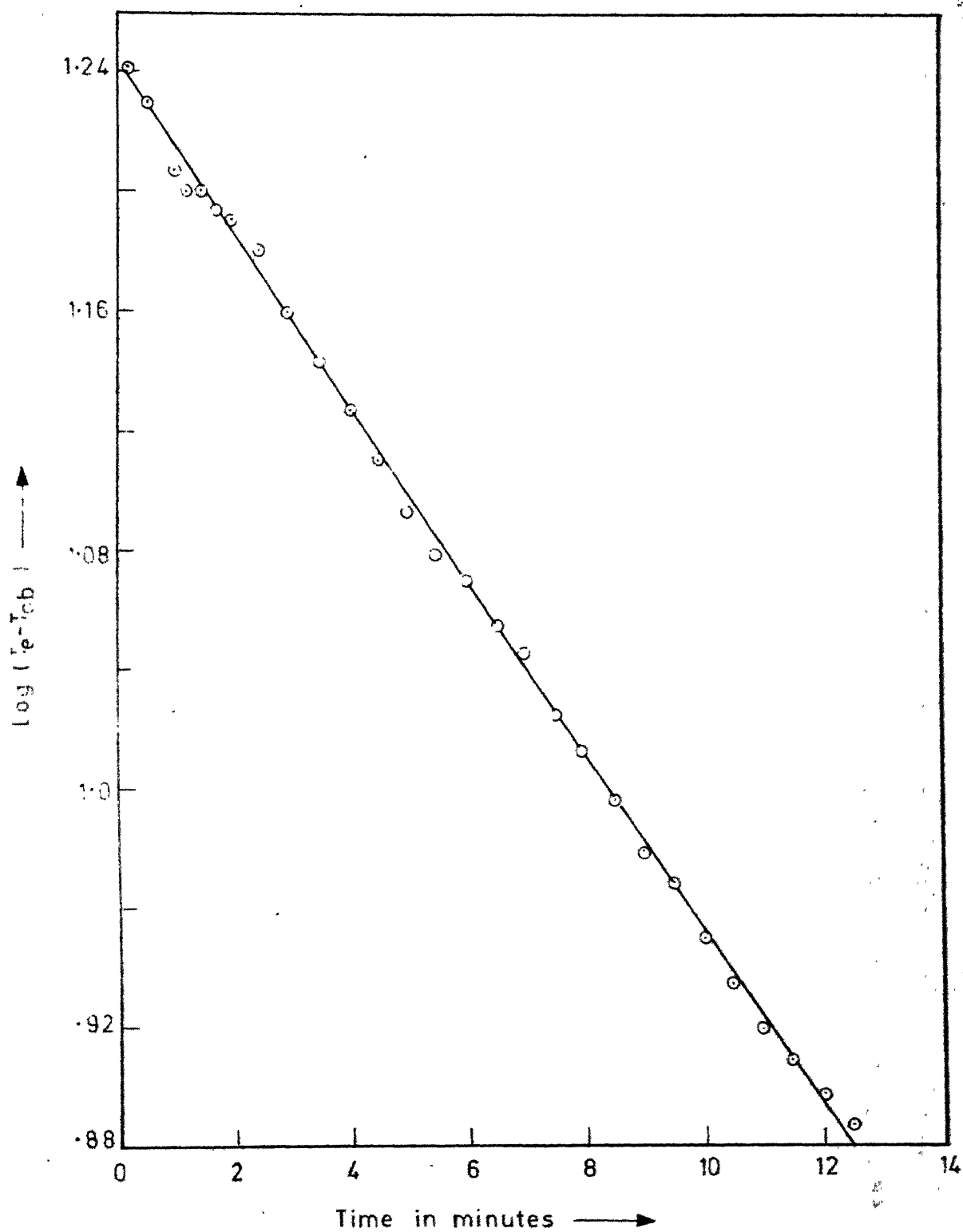


Fig. 10. Plot of $\log (T_e - T_{ob})$ against time for addition of a lead specimen.

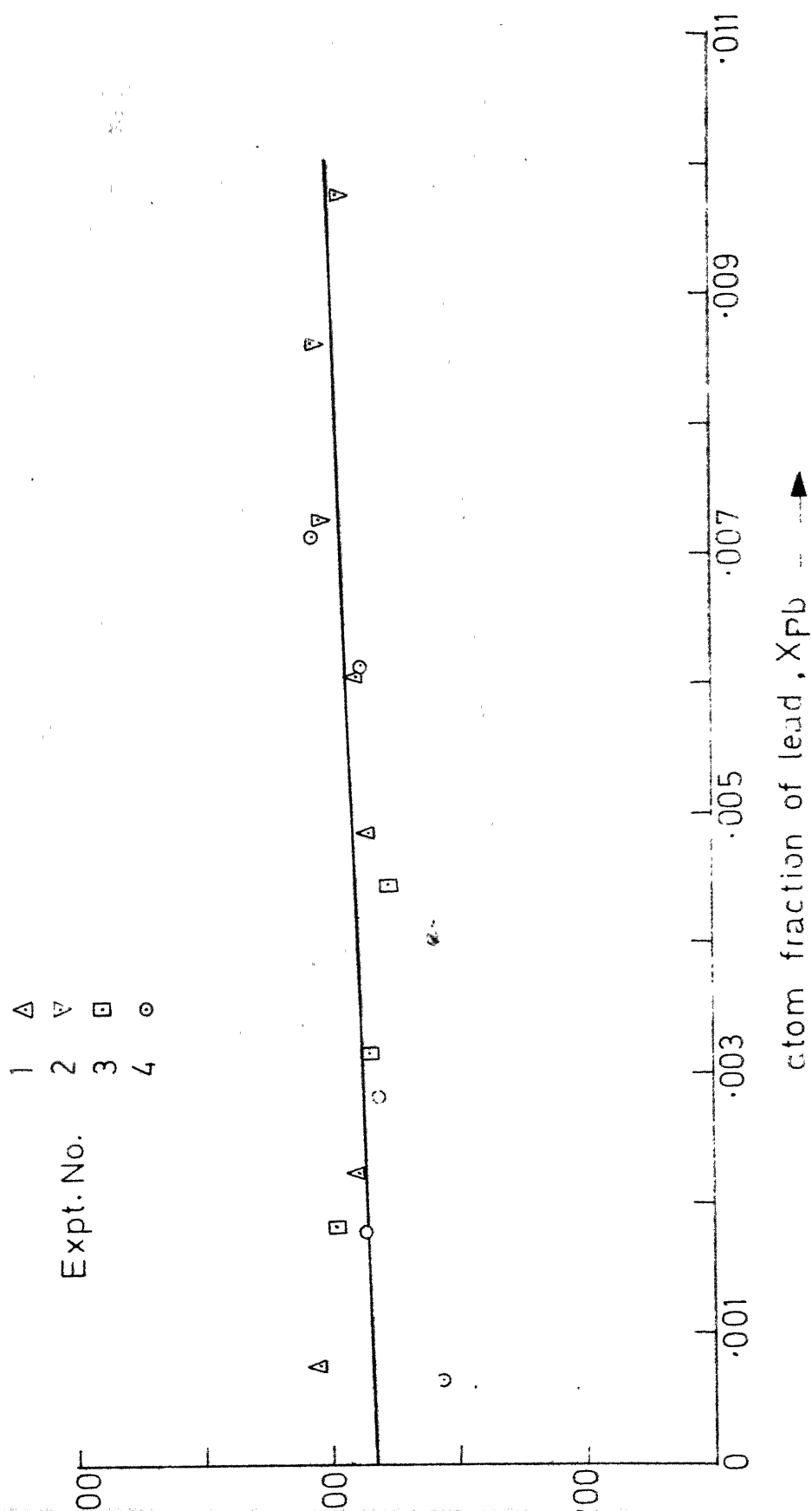


Fig. 11. Partial gram-atomic enthalpy of lead relative to solid lead in the bismuth-tin-lead solutions at 462°K as a function of atom fraction of lead ($X_{Sn}/X_{Bi} = 1.5$).

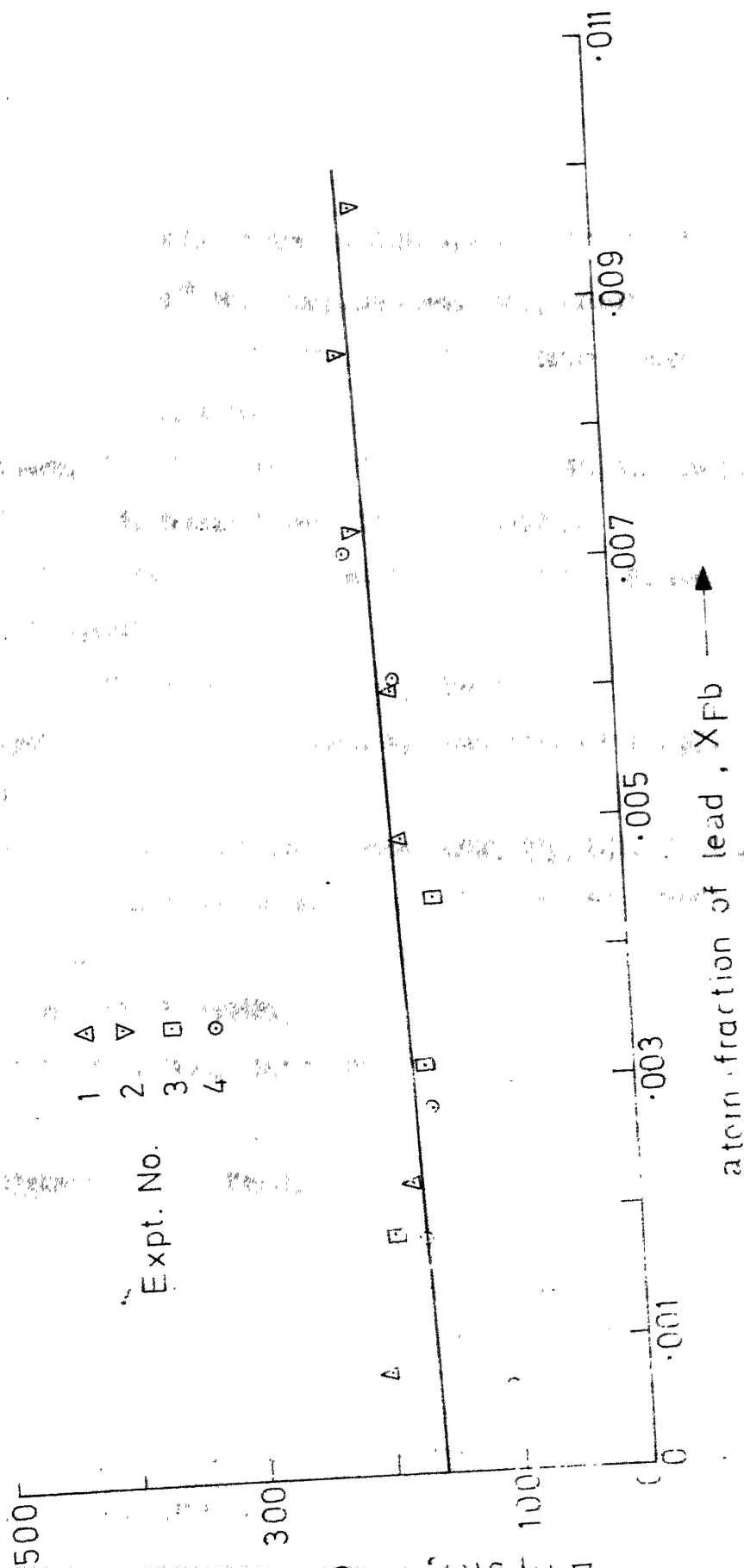


Fig. 12. Partial gram-atomic enthalpy of lead relative to liquid lead in the bismuth-tin-lead solutions at 462°K as a function of atom fraction of lead

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